

**IMPACTS OF TEMPERATURE AND HYDRAULIC
RETENTION TIME ON ODOURS PRODUCED FROM
AUTOTHERMAL THERMOPHILIC AEROBIC
DIGESTION**

by

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Abstract

Five different combinations of Hydraulic Retention Times (HRT) and temperatures were used in a two stage (feed and test reactor) Autothermal Thermophilic Aerobic Digestion System to assess the impact of these parameters on the production of odorous gases. The gases monitored were hydrogen sulphide, dimethyl sulphide, methyl mercaptan, ammonia, and amines. Other liquid parameters were also monitored in order to better understand the impacts of temperature and HRT. These parameters are total solids content, volatile solids content, volatile solids destruction, specific oxygen uptake rate, alkalinity, ammonia concentration, and pH. In order to assess the character of the sludge and understand the digestion process the carbohydrate, fat, and protein content were also measured in the inputs and in the test reactor.

It was found that all of the odorous compounds measured were affected by stage of digestion and temperature more than by HRT. Of the five compounds monitored, none were affected by changes in the HRT of the test reactor. However, the concentrations measured in the feed and test reactors were often a degree of magnitude apart. The reduced sulphur compounds (hydrogen sulphide, methyl mercaptan, and dimethyl sulphide) were found in higher concentrations in the feed reactor than in the test reactor; whereas ammonia and amines were found in much higher concentrations in the test reactor than in the feed reactor. Also, ammonia concentrations were significantly higher in both reactors when the temperature was higher; and amine concentration was higher in the test reactor when the temperature was higher. One set of tests for volatile fatty acid concentration was also undertaken.

While breakdown of the carbohydrates and fats occurred throughout the process, proteins were broken down into their amino acids, releasing reduced sulphur compounds in the feed reactor and then deaminated, releasing ammonia and amines in the test reactor.

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1 Introduction

1.1 Background

The cost of building and operating a wastewater treatment plant can be high and often the majority of these costs can be related to residuals management. In the past, sewage sludge was often taken to the nearest landfill or simply dumped into the ocean. Over the last few decades, these practices have become illegal in many areas because of their adverse effects on the environment. This has forced researchers and practitioners to discover new and innovative ways of treating sewage sludge. The result has been the discovery of processes such as Autothermal Thermophilic Aerobic Digestion (ATAD), which not only treats sewage sludge, but also pasteurizes it and produces a beneficial end product. According to Jewell and Kabrick (1980) “Wastewater sludge and other waste organics should be used for beneficial purposes, whenever such practices would be safe and cost effective. Implementation of this policy usually results in the application of sludge to agricultural land for soil property improvement or fertilization for crop production.”

ATAD is one of very few processes that are capable of producing biosolids, or treated wastewater sludge, that are safe for use in agriculture. Each ton of sludge contains approximately 40kg of Nitrogen, 70 kg of Phosphate, 70 kg calcium and 7 kg magnesium that could be used for fertilizing (Zwiefelhofer, 1985). By returning these nutrients to the natural cycle, one can partially reduce the need for artificial fertilizers (Zwiefelhofer, 1985).

Full-scale use of ATAD processes have been in use since 1977 in Europe (LaPara and Alleman, 1999) and, as of 1980, already 20% of sewage sludge produced in the U.S. was used in agriculture (Jewell and Kabrick, 1980). As of 1995, there were 50 operational ATAD systems in Canada and Europe (Burnett, 1995). It is anticipated that today there are over 200 systems worldwide.

The process at the Salmon Arm Wastewater Pollution Control Centre (WPCC), Salmon Arm, BC, Canada, consists of five reactors in series and is a retrofit design (Kelly, 1990). The layout of these tanks is as pictured in Figure 1 (all dimensions are in metres). Both primary and secondary sludge are fed into ATAD 4. The transfer process involves transferring from 3 to 2 or 1 for storage and cool down before centrifuging, then from 5 to 3, and finally from ATAD 4 to 5. Tank #6 is not in use presently. Since there are two storage tanks (1 & 2) and tank 2 is the smallest in the system, it was chosen to be the test reactor in this study.

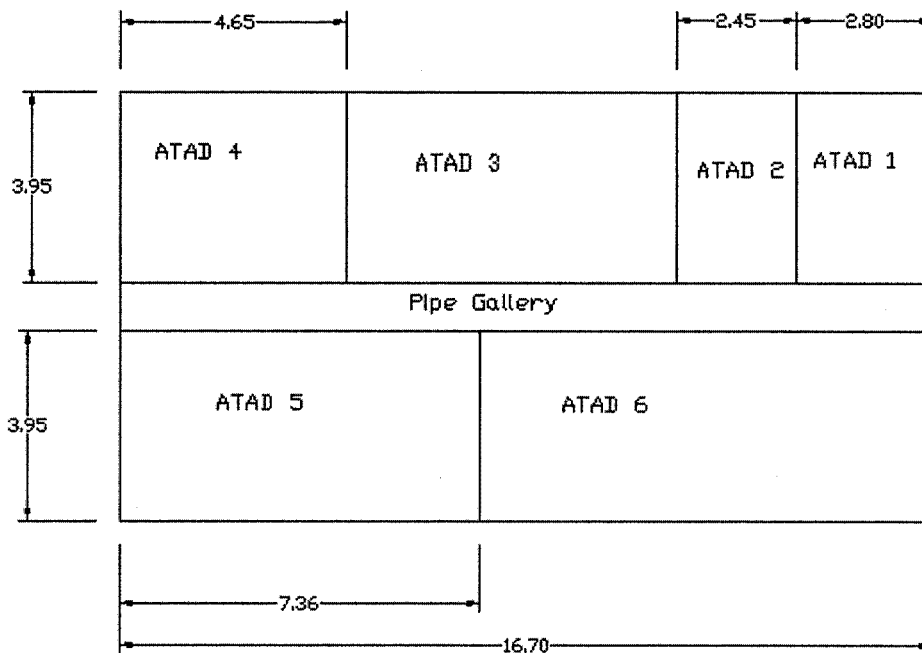


Figure 1: Plan view of Reactor Configuration at Salmon Arm WPCC

1.2 Research Objectives

The goal of this study is to test the effect that Hydraulic Retention Time (HRT) and Temperature have on the amount and type of odorous gases produced by the ATAD system. HRTs between 5 and 20d and Temperatures between 50 and 75°C were considered. The initial aim of this study was to set up a matrix with a combination of HRTs and Temperatures (such as Table 1) and test out as many combinations as

necessary, to gather the relevant information. To the author's knowledge, no similar field-based research had ever been carried out and reported.

Table 1: Matrix of Conditions to be Run

Temp. (°C)/ HRT (d)	5	10	20
50	X		X
60		X	
70	X		X

Another secondary aim of the study was to see, if possible, what were the effects on odour at very high temperatures (above 70°C). The Salmon Arm WPCC had very rarely experienced such high temperatures, so the challenge was how to achieve and maintain such temperatures.

2 Literature Review

2.1 Description of the ATAD Process

Autothermal Thermophilic Aerobic Digestion (ATAD) is a process used for the digestion of primary and secondary sludge produced through wastewater treatment operations. It has many advantages over other digestion processes and refers to a process that utilizes the heat produced through the breakdown of organics in wastewater to increase the temperature of the slurry (Jewell and Kabrick, 1980).

The ATAD process is called “autothermal” because it generates heat as it breaks down organics, thus enabling the process to be almost entirely self-heating. For every kg of volatile solids that are destroyed, approximately 20 000kJ of heat is produced (Tchobanoglous et al., 2003), depending on the relative content of carbohydrates, fats and proteins. However, the process is not completely autothermal, since mixing is required to supply some of the heating energy; approximately 25-30% (Kelly et al., 2003). The amount of mixing energy required is between 100 and 500 W/m³, depending on reactor shape, dimensions and temperature (Kelly and Warren, 1995).

The word thermophilic is an adjective that describes bacteria that thrive at above-normal temperatures, typically this means between 40 and 80°C. For biological wastewater treatment, thermophilic generally refers to any process operating above 45°C (LaPara and Alleman, 1999). ATAD processes are typically operated at temperatures between 45° and 65°C (Layden, 2007), but temperatures well over 70°C have been recorded (Kelly et al, 1993). These thermophilic temperatures can be achieved without external energy, even if the temperature of the feed sludge is as low as 0°C and air temperatures are as low as -10°C (Jewell and Kabrick, 1980).

The process is termed “aerobic”; however, it is rare for ATAD reactors to have any measurable dissolved oxygen and therefore would be more accurately described as microaerophilic. This environment encourages the growth and proliferation of facultative

microorganisms, allowing for oxidation and fermentation reactions to occur simultaneously (Kelly, 1990).

2.2 Benefits of ATAD

Although ATAD systems have poor bacterial flocculation and require tank aeration, foam control and odour treatment (Tchobanoglous et al., 2003), there are still many advantages to ATAD (LaPara and Alleman, 1999). The primary advantages of this technology are faster biodegradation rates, lower sludge yields, excellent process stability, more cost effective stabilisation, and quicker pasteurization than conventional sludge digestion processes (LaPara and Alleman, 1997 & 1999 and Ugwuanyi, 2007).

The ATAD process has also been proven to be particularly effective in small communities (Kelly et al., 1993) and is used to treat not only municipal sludge, but also livestock, slaughterhouse, brewery, synthetic, and citrus fruit processing wastewaters (LaPara and Alleman, 1997).

2.2.1 Reaction Rates

Because of the high temperatures that ATAD reactors operate in there are increased rates of oxidation, often resulting in smaller digester volumes; this leads to cost savings (Jewell and Kabrick, 1980). Substrate is utilized 3-10 times faster in thermophilic processes than in mesophilic processes (LaPara and Alleman, 1999). Also, the HRTs are much lower than those typically used for mesophilic digestion and the capital cost of a thermophilic system is reduced, in comparison to a mesophilic system.

The primary aim of any sewage sludge digestion process is to stabilize and reduce the amount of solids that must be managed. The ATAD process is known to reduce total and volatile solids more quickly and effectively than other processes, because enzymes from thermophilic bacteria can more easily hydrolyze cellular components from secondary sludge than bacteria that thrive under other conditions (Kim et al., 2002). A 40 to 60% reduction in volatile solids is not uncommon for these systems (Kelly et. al., 1995). However, ATAD typically has sludge production rates similar to those of

anaerobic processes, because of increasing k_d and k_{max} values (growth rates) at higher temperatures (LaPara and Alleman, 1997 and 1999).

2.2.2 Stability and Pasteurization

ATAD processes are inherently suitable for organic digestion because of the ability of thermophiles to “metabolise a wide variety of organic compounds” (Ugwuanyi, 2007). Also, rapid recovery is possible from upset conditions because of the high degradation rates (LaPara and Alleman, 1999).

ATAD is capable of, not only reducing pathogens in sludge, but total pasteurization; this allows for unrestricted end use of the biosolids. In order for biosolids to be used in agriculture, they must be Class A as defined by USEPA Rule 503. Class A biosolids are defined in the US as containing less than 3 Most Probable Number (MPN) of *Salmonella* sp. per 4 grams of total dry solids, or 1000 MPN of fecal coliform per gram of total dry solids, and very low levels of metals (Kelly and Warren, 1995). In British Columbia, Canada, only the coliform criteria is applied. The ATAD process is even more common in Germany than in Canada, where the standard is a non-detectable levels of pathogens in biosolids (Burnett, 1995).

2.3 Operating Conditions

2.3.1 Temperature

ATAD systems operate on the same principle as composting: heat is produced from the breakdown of organics in the presence of oxygen (aerobic oxidation) which results in high reactor temperatures; this in turn, results in pathogen destruction and more breakdown of organics (LaPara and Alleman, 1999 and Kelly and Warren, 1995).

The temperatures achieved depend on oxygen supply and availability of metabolizable carbon and energy sources (Ugwuanyi, 2007). If lower levels of degradable organics were used than are available in wastewater sludge or lower feed rates, this process would require external heating and not be cost-effective (LaPara and Alleman, 1997). Sometimes heat exchangers are used to preheat and/or cool the sludge,

to improve the efficiency of the process (Burnett, 1995); however, heating of the bulk liquid would be inefficient.

Temperature is also affected by foaming. Foam is typically produced as mesophilic bacteria are replaced by thermophilic organisms during temperature increases, generally between 40 and 50°C (Kelly and Warren, 1996). Foaming provides some insulation and assists in maintaining a thermophilic process.

Even more significant impacts on temperature are sometimes caused by changes in the feed, either in the character of the organic content or the rate at which it is fed to the reactor (Kelly, 1996). Feed rates and composition affect temperature, as this is the source of the organics that are metabolised and result in heat production. For this reason, it can be difficult to achieve high temperatures for longer HRTs. Maximum temperatures are achieved by supplying sufficient oxygen for metabolism of the organics, while minimizing the heat lost in the exhaust air (Tchobanoglous et al., 2003).

2.3.2 Aeration

Oxygen can be supplied through aerator-mixers that draw in air as they rotate. Their high speed of rotation in the sludge can create extremely small bubbles that are thought to be responsible for high oxygen transfer efficiencies (Jewell and Kabrick, 1980). Higher transfer efficiencies mean that smaller volumes of air are required (Kelly, 1996) which leads to cost savings. Typically minimum oxygen transfer efficiencies of 10-20% are required to achieve thermophilic temperatures (LaPara and Alleman, 1999).

Although the solubility of dissolved oxygen decreases as temperature increases, the changes in viscosity and diffusivity that occur are such that the overall oxygen transfer rate is not greatly affected (LaPara and Alleman, 1997). Typically, at least 0.5 to 1.5 volumes of air per volume of tank per hour are needed (Kelly et. al., 1995); these are the same rates used for mesophilic aerobic digestion, however these tanks are usually two to four times larger, and therefore require a much larger quantity of air (Kelly, 1990).

Providing more air can increase the temperature but there is a threshold beyond which the result of excessive airflows is a drop in temperature, often below the necessary level for pasteurization. To compensate for this loss of heat, more mechanical or mixing energy is used (Kelly, 1996). However, if insufficient air is supplied, high oxygen uptake rates (OUR) can result; these are difficult to measure because of the high amount of microbial activity. There is potential for the activity to be so great that the oxygen demand cannot be met by commercially available equipment (LaPara and Alleman, 1997).

Typically ATAD systems operate with Oxidation Reduction Potential (ORP) values between -550 and +150 mV (Staton et al., 2001), which indicate very low dissolved oxygen. At start-up or in the first cell of the process (Kelly, 1991) the reactors are normally in the lower end of this range (Kelly et. al., 1995). This range is suggested as beneficial, as it maximizes the oxygen transfer efficiency (Kelly, 1990). Use of pure oxygen in ATADs was investigated and is desirable, but it was found to be unnecessary (Kelly, 1990). It is suspected that adding an excessive amount of pure oxygen destroys the balance of oxidative and fermentative reactions that makes the digestion process so effective. ORP is used to predict odours, aeration deficiencies, and inadequate mixing (Kelly, 1991).

2.3.3 Bacterial Diversity

Since most other sludge digestion processes operate at mesophilic temperatures, very little is known about the microbial species and diversity that ATAD reactors support. Many of the bacteria commonly found in mesophilic processes are not present in thermophilic aerobic conditions, such as nitrifying and floc-forming bacteria or protozoa; instead, ATAD reactors tend to be dominated by thermophilic bacilli that have unique nutritional requirements (LaPara and Alleman, 1999) and a higher rate of metabolism (Burnett, 1995). It has also been noted that, as temperature increases, the number of competing strains decreases (Kelly, 1990). Sonnleitner and Fiechter (1985)

found that 95% of the thermophiles in an aerated thermophilic sludge digestion process were *Bacillus stearothermophilus*.

Sonnleitner and Fiechter (1985) found that, although ATAD reactors generally have a basic pH, there are always both acidophilic and alkalophilic thermophiles present. They also found that there was a broad thermal distribution, from psychrophiles to microorganisms capable of growth at 80°C (extreme thermophiles) for HRTs between 10 and 47h. Partly because of this distribution, the thermophilic microorganisms were found to be able to withstand large changes in temperature, retention time, and aeration rate. They also grew rapidly on simple media, even in oxygen-limited conditions. However, more viable cells were found when the process was operated under constant conditions than after drastic changes and there were generally higher numbers of viable cells at lower temperatures (55°C versus 70°C) and higher pHs.

2.3.4 Hydraulic Retention Time

ATAD systems are often operated using several reactors in series, in order to provide flexibility; with a wide variety of configurations, retention times, and operating temperatures. Using several reactors in series also allows the system to operate using plug flow like conditions. A key gap in ATAD research is optimum operating conditions including temperature, dissolved oxygen concentration, and pH (LaPara and Allema, 1999).

Besides temperature and air, the most important variable in ATAD processes is sludge age or HRT (Kelly et al., 1995). The total HRT of an ATAD system typically ranges between 5 and 15d (Kelly and Mavinic, 2003). The HRT chosen is dependant on the amount of solids destruction desired, which is directly related to the product of reactor temperature (°C) and HRT (d); 400°C-d is considered a design minimum for most ATAD systems (Kelly, 1991). Therefore, there can be fairly wide variability in HRTs, depending on the temperature of the reactors and the factor of safety to be used (Burnett, 1995).

Many ATAD systems in Europe use HRTs of only 3 to 5d and are able to meet the pathogen requirements (Kelly, 1990). In the United Kingdom, for stability to be achieved, a minimum HRT of 7d is recommended, as long as the sludge has reached 55°C for at least 4h (Kelly, 1990). One of the benefits of using multiple reactors in series is that for thermophilic processes, *E. coli* have been found to be totally inactivated, such that no regrowth occurs after centrifuging (Higgins et al., 2006). Also, it has been shown that more stabilization occurs when the digestion period is longer (Kelly, 1990). This directly impacts the quantity and quality of odours produced, as will be discussed later.

2.3.5 Stability

Stability of digested biosolids can be measured in various ways, including volatile solids reduction, total solids destruction, pasteurization, specific oxygen uptake rate (SOUR), and odour acceptability. These same parameters can also be used to measure the effectiveness of a digestion process (Kelly, 1990). Any large variation in these parameters is typically caused by a change in the feed. However, for assessing reactor state, temperature and ORP are the most valuable parameters (Kelly, 1990). Typically, sludge is deemed stable if the temperature-corrected SOUR value is between 0.5 and 2 mg O₂/g/h (Kelly, 1990). USEPA 503 regulations allow a criteria for stability of less than or equal to 1.5 mg O₂/g-h at 20°C or greater than 38% volatile destruction (USEPA, 2003). It is clear, however that the production of odour is also a measure of stability. No odour, after biological treatment and conditioning, would indicate a stable product. The use of the 38% volatile destruction as a measure of stability may need to be questioned.

2.3.6 Feed

ATAD systems can be operated using continuous, semi-continuous or batch feeding. However, Sonnleitner and Fiechter (1985) suggest that the rapid metabolism of thermophiles can only be exploited in continuous cultures.

Although both primary and secondary solids can be digested in an ATAD system, secondary sludge is more readily biodegradable (Layden, 2007) and considered to be in

the same oxidative state as the thermophiles (Kelly, 1990). The carbohydrate, protein, and fat content of the sludge affects how much oxygen is required to fully oxidize the waste, since fat requires more oxygen than protein or carbohydrate. Theoretically, about 2.9 kg O₂ is required to oxidize every kg of fat, 1.65 kg O₂ for each kg of protein, and 1.6 kg O₂ per kg carbohydrate (Kelly, 1990).

Typically, in untreated domestic waste sludge, carbohydrates make up about 34%, proteins 29%, and fats 28% (Kelly, 1990). Secondary, or waste biological sludge requires less oxygen per gram than primary sludge to oxidize, as it is in a form that is more bioavailable; however, overall, it has a lower volatile content and decreases further with age. Overall, the feed should have between 3 and 7% solids with an average of 5% (Kelly et. al., 1995 and Burnett, 1995). The feed concentration can have an effect on temperature as concentrations above 6% can result in oxygen-limited conditions (Layden, 2007), which can lead to odour issues. Higher solids concentrations can also limit the mixing ability of commercially available mixers.

2.3.7 pH, Alkalinity and Protein

Typically ATAD reactors have a relatively high pH, between 7 and 9 (Jewell and Kabrick, 1980 and Tchobanoglous et al., 2003). The pH of an ATAD reactor is also linked to the ammonia and nitrogen content and the high pH is suspected to be related to the inhibition of nitrification at temperatures above 43°C (LaPara and Alleman, 1997). It has also been proposed that nitrogen content decreases with digestion and is released as ammonia gas (Kelly, 1990).

Alkalinity is an important parameter because increases are related to ammonia formation due to the breakdown of organic nitrogen, which, in turn, is linked to protein content (Kelly, 1990). Ammonia gas is commonly detected from ATAD reactors, which confirms that this breakdown is occurring. Ammonia is a source of alkalinity because it is a weak base that can buffer acids. Acetic acid can also be present in these reactors and can act as a buffer (Kelly, 1990). Another source of alkalinity can be hydrogen sulphide,

since it is a weak base. However, temperature also plays a role as the dissociation constant of H_2S increases with temperature (Yongsiri et al., 2004), such that at higher temperatures it dissociates in the liquid rather than going into the gas phase. Carbon dioxide, which dissociates into carbonic acid (a weak acid that is a major source of alkalinity), is less soluble with increasing temperature meaning that at lower temperatures there is more in solution, and potentially higher alkalinity. Because of this, alkalinity in ATAD systems has been measured as high as 2000 mg/L $CaCO_3$.

Since protein degrades at a slower rate than other macronutrients, ATAD systems are also known for the accumulation of protein. This is caused by “the selective degradation of carbohydrate [and fat], resulting in the loss of carbon,” which results in a relative accumulation of nitrogen as protein (Ugwuanyi, 2007). Ugwuanyi (2007) also argues that the protein content of some thermophilic bacteria can be manipulated by changing temperature and aeration. As proteins are degraded in ATAD systems, acetate is formed which can be odorous. If there is sufficient dissolved oxygen, the acetate will be oxidized (Tchobanoglous et al., 2003). Proteins are a large concern with respect to odour generation and partial degradation can be problematic.

Of the macronutrients (carbohydrates, fats, and proteins) protein is the only one that contains sulphur. Therefore, the odorous reduced sulphur compounds that are often associated with ATAD systems are directly related to the protein content of the sludge. Although healthy individuals excrete low levels of protein, bacteria in the wastewater treatment process can absorb this protein and the content can actually increase as the biomass grows, before reaching the digestion system. As well, unhealthy individuals can sometimes excrete higher levels of protein and this can affect the treatment process in communities with a higher number of such individuals.

2.4 Odour Issues

One of the main problems encountered with ATAD systems is objectionable odour. Some of the common odours include mercaptans, dimethyl disulfide, dimethyl sulfide,

hydrogen sulfide, ammonia and volatile fatty acids (VFA) (Kelly et al., 1995). These characteristic odours result from sulphur and amines, which are simply a byproduct of bacterial metabolism (Integra Engineering, 1997). They also represent protein building blocks.

Odours are typically dealt with through biofilters and chemical scrubber systems, but sometimes these systems are inadequate (Bowker and Trueblood, 2002). There are many factors that contribute to the odours produced and their concentration, but little work has been done specifically in this area. The issue of odours is an important one because of its potential health effects and because even very low concentrations (ppb) of some gases can be easily detected by the human nose (Kelly et al., 2002). Prolonged exposure to even low concentrations of odorous gases can cause fatigue, headaches, and effects on mood and attitude, as well as other physical effects (Integra Engineering, 1997b). Methyl mercaptan is toxic at very high concentrations and can affect the central nervous system. These odours can also be difficult to treat because they can be a combination of many different gases, each having different oxidation kinetics (Kelly et al., 2002).

It has long been suspected that odours are related to improper mixing and aeration devices (Kelly, 1990). Others have observed that odours are related to temperature (Layden and Bartlett, 2007), VFA concentrations, pH, ORP (Kelly, 1990) or specific microorganisms (Kelly et al., 2002). It has been observed, however, that the odour magnitude is greatest when the airflow rate is lowest (Kelly et al., 1995), showing that there must be some relationship to aeration. Regardless, all of these other parameters are also related to the oxidation condition. If there is insufficient mixing and aeration, the system can become anaerobic, thus resulting in a different microbial makeup in the reactor, high VFAs, low ORP, high pH, and this can also have various effects on temperature.

According to Kelly and Warren, 1995 and Kelly, 1990 the first digester in the process has higher concentrations of nitrogenous compounds and ammonia, and a higher

pH. Later reactors tend to have higher concentrations of dimethyl sulfide and dimethyl disulfide as reduced sulphur compounds, such as mercaptans, are oxidized.

2.4.1 Odour and Air

Another important parameter that affects odour production and the process, in general, is air supply. Too much aeration can result in cooling and too little or improper aeration or mixing can cause incomplete oxidation of organics and can keep the system from achieving higher temperatures. Most ATAD systems have no constant aeration speeds and there is no way to vary the amount of air supplied separately from the mixing speed (Staton et al., 2001).

Incomplete oxidation can cause odorous compounds such as amines and ammonia to be released (Kelly et al., 2003). Kelly et. al. (1993) recommend keeping the air supply between 0.5 and 2.0 v/v-hr to avoid incomplete oxidation or cooling. It is also known that fine bubbles are important for oxygen transfer and pure oxygen can also be used (Kelly and Mavinic, 2003).

FUCHS aerators or Turborators® (aerator-mixers) are the most popular aeration devices used in ATAD systems. Both of these technologies provide air and mixing at the same time. One of the common problems with these aerators is fouling, which can have significant effects on digestion efficiency and temperature (Layden, 2007). Other devices include Venturi-aerator and mixers and jet aerator mixers with blowers (Kelly and Warren, 1995 and Layden, 2007).

Some of the important odorous compounds mentioned above are related to each other as oxidation products of other compounds. When methyl mercaptan is oxidized, the products in order of their oxidation are dimethyl sulphide (Kelly, 1990), dimethyl disulphide, carbonyl sulphide, water, and carbon dioxide. Jee and Tao (2006) suggest that oxidation of these reduced sulphur compounds happens more readily with nitrate than with oxygen, although there is little additional evidence in the literature to support

this claim and in an ATAD system there is no nitrate available because of the high temperatures.

2.4.2 Odours Produced

ATAD systems do not generally operate under truly aerobic conditions (measurable dissolved oxygen), and hence large amounts of ammonia and reduced sulphur compounds can be produced (Bowker and Trueblood, 2002). The most common problem odours produced by ATAD systems are hydrogen sulphide, reduced sulphur compounds, mercaptans, ammonia, and amines.

Mercaptans, dimethyl sulphide, and dimethyl disulphide are especially difficult to treat because of their higher molecular weight, they are also quite malodorous (Bowker and Trueblood, 2002). Staton et al. (2001) point out that many ATAD units demonstrate anaerobic off-gas problems because they produce elevated levels of mercaptans and hydrogen sulphide. It is understood that sulphate-reducing bacteria produce hydrogen sulphide and mercaptans, as they break down proteins in an anaerobic environment (Integra Engineering, 1997). Sulphate reducing bacteria are only present when there are significant concentrations of sulphate in the wastewater and they are obligate anaerobes. Therefore, the more anaerobic the environment, the more likely it is to have these organisms present and producing these problem odours.

Although the literature contains some information on what types of odours can be expected from ATAD systems, there is very little published on the odorous gases and the concentrations produced from ATAD systems. An evaluation of the odour treatment process was done and the results published from two plants operated by the Eagle River Water and Sanitation District in Colorado, USA. These facilities were considered to have some of the most advanced odour collection and treatment operations in North America (Kelly et al., 2002). According to this study, the most problematic odorous compounds were methyl mercaptan, hydrogen sulphide, dimethyl sulphide, dimethyl disulphide, carbonyl sulphide and ammonia (Bowker and Trueblood, 2002).

Ammonia is a common off-gas as a result of ammonia stripping due to basic pHs (Staton et al., 2001). High levels of ammonia and low levels of reduced sulphur compounds have been empirically linked to a 'healthy' reactor (Staton et al., 2001), although no data are provided to substantiate this claim.

Oxidation Reduction Potential (ORP) indicates the oxidative state of the process. Negative ORP values indicate anaerobic conditions that are reducing conditions that support the production of hydrogen sulphide and other odorous compounds, such as reduced sulphur compounds and volatile fatty acids (Scisson, 2006). Hydrogen sulphide produced from sulphate reduction happens most favourably at ORP values between -200 and -300 mV (Kelly, 1990). A study done by Kelly et al. (1993) notes that there was no correlation between ORP and temperature, but that odours seemed worse with lower ORP values. Because ATAD systems tend to operate at low or negative ORP values, this is likely one of the reasons for high concentrations of odorous compounds, at least in the first reactor(s).

3 Methods and Materials

3.1 Salmon Arm Wastewater Pollution Control Centre

This study was carried out at the Salmon Arm Water Pollution Control Centre (WPCC), because it employs an ATAD system; and because the facilities are accessible and the City of Salmon Arm has encouraged the use of the water pollution control centre for research.

The Salmon Arm WPCC uses primary settling and a trickling filter suspended growth process, to provide biological nutrient removal (Kelly, 1991). The ATAD reactors are fed a combination of primary sludge and waste trickling filter activated sludge (TFAS) solids. The ATAD system at Salmon Arm consists of six reactors, one of which is not in use and two that are used for storage before centrifuging. The feed reactor is fed primary solids continuously and TFAS semi-continuously. Mixing and aeration are provided by Turborators ®.

Under normal operation of the ATAD system, primary sludge is fed to the feed reactor (ATAD 4) every hour and TFAS is pumped to the feed reactor when the standpipe it is stored in is full (approximately twice per hour). The amount of TFAS fed to the ATAD system is highly variable because of sloughing events in the trickling filter.

The ATAD transfer process occurs twice daily. To provide digestion capacity, the transfer process begins with a withdrawal of sludge from ATAD 3 and transfer to ATAD 1 or 2, for storage and cooling. Following this withdrawal, sludge is transferred from ATAD 5 to ATAD 3 and then finally from ATAD 4 to ATAD 5. ATAD 4 is then fed with fresh sludge. This results in a semi-batch process as noted by Kelly and Warren (1996). Figure 2 gives a diagrammatic overview of the process.

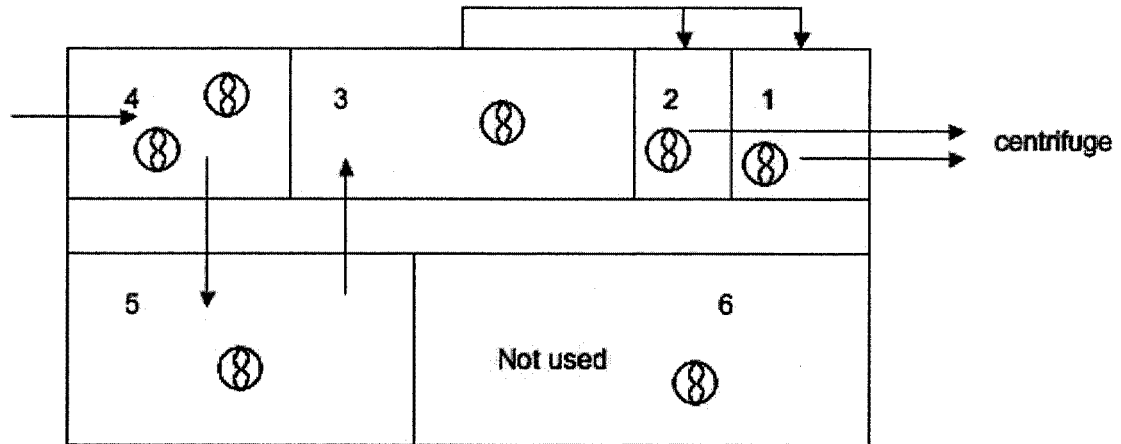


Figure 2: Transfer Process Diagram

The reactor used in this study was ATAD 2, which is normally used as a storage reactor. The reactor has dimensions of 2.45m by 3.95m, giving it a cross-sectional area of 9.68m². The tank has a depth of approximately 3m and a minimum depth of 2.2m of solution must be kept in the reactor, to ensure that the Turborator is kept in solution.

The Turborator used in ATAD 2 to supply air and mixing has a 7.5 HP motor with a motor speed of 1745rpm and a Turborator speed of approximately 1200 rpm at full speed. The feed reactor had two Turborators, one with a 7.5 Hp motor and one with a 10Hp motor. The 10Hp motor had a max speed of 1750 rpm and a max Turborator speed of 1100rpm, while the 7.5 Hp motor was identical to the one in ATAD 2.

3.2 Operating Conditions

The two parameters that were manipulated in this study were Hydraulic Retention Time (HRT) and temperature. It was discovered early on in the study that, for statistical reasons, most, if not all, of the conditions in the matrix shown in section 1.2 would have to be run for the results to be comparable. Because of time constraints, it was decided to reduce the matrix to a 2x2, using only the longer HRTs and to do only one other run at a shorter HRT.

3.2.1 Hydraulic Retention Time (HRT)

HRTs between 5 and 20d were to be tested. HRT is controlled by the flow rate and volume of the reactor. Since continuous flow to the reactor was not possible, to mimic the operation of the plant, and for simplest operation, feeding once or twice a day was considered. If ATAD 2 were to be operated under conditions that are similar to the operating conditions of the plant, it would need to be fed twice a day from ATAD 4.

The amount to be fed to ATAD 2 per feeding can be calculated based on the HRT desired and the number of feedings during the retention time. HRT is calculated using Eq. 1.

$$\text{HRT} = \frac{\text{Volume}}{\text{Flow Rate}} \quad (\text{Eq. 1})$$

However, the total retention time experienced by the sludge must also include the time in the feed reactor (ATAD 4). Because of the way ATAD 4 is dosed, hourly with primary sludge and periodically with TFAS, the HRT is always changing. The HRT of ATAD 4 was estimated using the average level in the tank and the amount of sludge fed to it each day. The average level in the reactor was used to calculate the volume of sludge in the reactor and the total amount of sludge it had been fed per day was monitored by the System Control And Data Acquisition (SCADA) system, to obtain the feed rate.

Once the HRT in ATAD 4 was determined, this number could be subtracted from the total HRT desired to get the required HRT in ATAD 2. Since the estimated HRT of ATAD 4 changes everyday, the HRT in the test reactor must also change, in order to maintain a constant overall HRT. The average HRT of ATAD 4 was approximately 4d.

A constant depth of 2.6m was maintained in the test reactor at all times, except during the short period of wasting and feeding, so that the volume in the tank was constant. Knowing the HRT and reactor volumes, the feed rate could be calculated. The feed volume could be translated to a change in depth by simply dividing by the cross-sectional area. For long HRTs, the depth of fluid to be drained was small. Because the

level in the ATAD tanks could only be determined to the nearest centimetre, it was decided to do one transfer per day, in order to be as accurate as possible. An example calculation is shown below.

$$\text{Total HRT} = 20\text{d}$$

$$\text{HRT in ATAD 4}$$

$$\theta = \frac{2.80\text{m} * 18.37\text{m}^2}{204242\text{L} / \text{d}} = 2.52\text{d}$$

$$\text{HRT in ATAD 2}$$

$$\theta = 20\text{d} - 2.52\text{d} = 17.48\text{d}$$

$$\text{Feed Rate} = \frac{\text{Volume}}{\theta}$$

$$\text{Feed Rate} = \frac{2.6\text{m} * 9.68\text{m}^2}{17.48\text{d}}$$

$$\text{Feed Rate} = 1.44\text{m}^3 / \text{d}$$

$$\Delta \text{depth} = \frac{1.44\text{m}^3 / \text{d}}{9.68\text{m}^2}$$

$$\Delta \text{depth} = 0.15\text{m} / \text{d}$$

It can be seen from this example calculation that, if two transfers were done per day, the change in the level in the tank could be less than 10 centimetres. Because of the accuracy of the level indicators, it was decided that it was better to only do one transfer to the test reactor per day.

3.2.2 Temperature

Temperature is typically the most important parameter to monitor in an ATAD system because it is correlated to pasteurization and because fluctuations can easily occur. Pasteurization is achieved by maintaining high temperatures for sufficient time to kill or inactivate pathogens. In this study, temperature was one of two key parameters adjusted, in order to achieve the various conditions.

One of the aims of the study was to see what were the maximum temperatures the system could maintain. The first condition to be tested was at the highest temperature, since it was the warmest time of the year (summer) and hence, higher temperatures would

be easier to achieve. The Salmon Arm WPCC also experiences more consistent operation during the summer than the winter.

Initially the Turborator in ATAD 2 was run at 100% of its speed, in order to reach the highest possible temperature. However, it was found that, after the initial oxygen demand was met, the temperature started to drop. At high temperatures, high airflow caused by the Turborator running at full speed, can result in higher evaporative losses, which causes drops in temperature and even volume, in the reactor (Kelly, 1990).

Once this was discovered, the speed of the Turborator was reduced but the temperature did not completely recover. In order to limit the amount of air being supplied to the reactor, the size of the opening in the Turborator was reduced. However, the result of this was not a reduced air supply, as desired, but rather the airflow velocity increased through the smaller opening, supplying the same amount of air. Following this, a system was devised where the air could be blocked for part of the day, while mixing energy was still delivered. During these hours, the air supply to the Turborator in ATAD 2 was blocked and the Turborator ran at 75 to 80% of its full speed. This allowed mechanical energy to be added, which resulted in higher temperatures but impeded the high airflow that would eventually result in temperature decreases. Since the transfer to the test reactor was done at approximately the same time everyday, it was decided that after the transfer, when more air was needed to satisfy the oxygen demand of the newer sludge, the Turborator would be run open to the atmosphere at 100% of its speed for several hours or until the temperature started to drop. This was done for two to six hours a day. After this, a cap was placed on the Turborator so that it would provide mixing energy without air. The cap would remain over the opening to the reactor until the following days transfer.

In other runs where a lower temperature was desired (55°C), the PLC Control system automatically increased or decreased the Turborator speed, to ensure the temperature in the reactor was within one degree of the desired value. This could be done without capping the Turborator. On average, the Turborator ran at about 40% of its

maximum speed. Except at very high temperatures, temperature can be increased by turning aerators or mixers up and decreased by turning them down.

3.3 Experimental Design

The experiments tested five different combinations of HRT and Temperature, as was originally planned. However, the combinations to be tested were changed as the experiment progressed.

To begin each condition, the test reactor was drained as far as possible. It would then be filled with “fresh” sludge from ATAD 4 (average HRT of 4d). The Turborator was initially run at full speed to encourage biological heat production until the desired temperature was reached. Daily wasting and filling of the tank occurred each morning following the filling day, to achieve the desired HRT.

In total five conditions were tested. Each run is described below.

Exp.# 1	3d	@	46C	+	17d	@	71C	≈	20d@67C
Exp. #2	3d	@	45C	+	4d	@	67C	≈	7d@58C
Exp.# 3	4d	@	46C	+	10d	@	64C	≈	14d@59C
Exp.# 4	3d	@	37C	+	17d	@	55C	≈	20d@52C
Exp.# 5	4d	@	33C	+	10d	@	61C	≈	14d@53C

Five gas concentrations and several liquid parameters were measured once the reactor was thought to have stabilised. Temperature, and ORP were measured continuously through the SCADA system. For most of the conditions, samples were taken several times a week and tested for total and volatile solids content, overall volatile destruction, and oxygen uptake rate to assess the stability of the reactor. Once approximate stability was achieved, all parameters of interest were measured on five separate testing days for each condition. On testing days, samples from ATAD 2 were analyzed for SOUR, total and volatile solids content, alkalinity, ammonia, and pH. A small sample would also be sent for proximate analysis, which includes moisture, ash, carbohydrate, protein, fat, and energy content. Samples of crude and TFAS were taken

for solids testing and proximate analyses on the same days as the ATAD 2 samples for those tests.

The five gases were also monitored on the test days. The gases measured were: hydrogen sulphide, ammonia, amines, methyl mercaptan, and dimethyl sulphide. These were measured both in the feed reactor (ATAD 4) and the test reactor (ATAD 2).

Quality Assurance and Quality Control were maintained by taking duplicate measurements of each parameter at least once, per testing cycle. This required duplicating one gas measurement and one liquid measurement from each source each testing day.

Samples of ATAD 2 liquid were taken in the morning, before the transfer was done, to ensure that the samples were representative of the previous days activity and did not include any fresh sludge. The samples were taken using a long, metal, sampling rod and the tests were done immediately. When it was not possible to do the tests immediately, the samples were stored in a fridge until the tests could be carried out (maximum 24h).

Gas concentrations were measured directly from the headspace of the reactors. Gas samples were taken on testing days in the afternoon, between 1 and 4pm, at least two hours after the daily transfer had been completed.

3.3.1 Stability

A conservative estimate for achieving steady state in a biological reactor is 2 HRT. Stability can also be measured using Specific Oxygen Uptake Rate (SOUR), percent volatile solids content, and volatile solids reduction. For the first two conditions tested, at least two HRT were allowed to elapse before testing began. For the other conditions the parameters mentioned above were monitored until stability was observed. The reactors were always given a minimum of one HRT to stabilize.

Figure 3 shows the variation in percentage volatile solids content in ATAD 2 over the length of the run. It is clear that the results are fairly sporadic, even after more than

two HRT have elapsed (see 20d@67C). However, for 14d@59C and 20d@52C stability seems to have been reached.

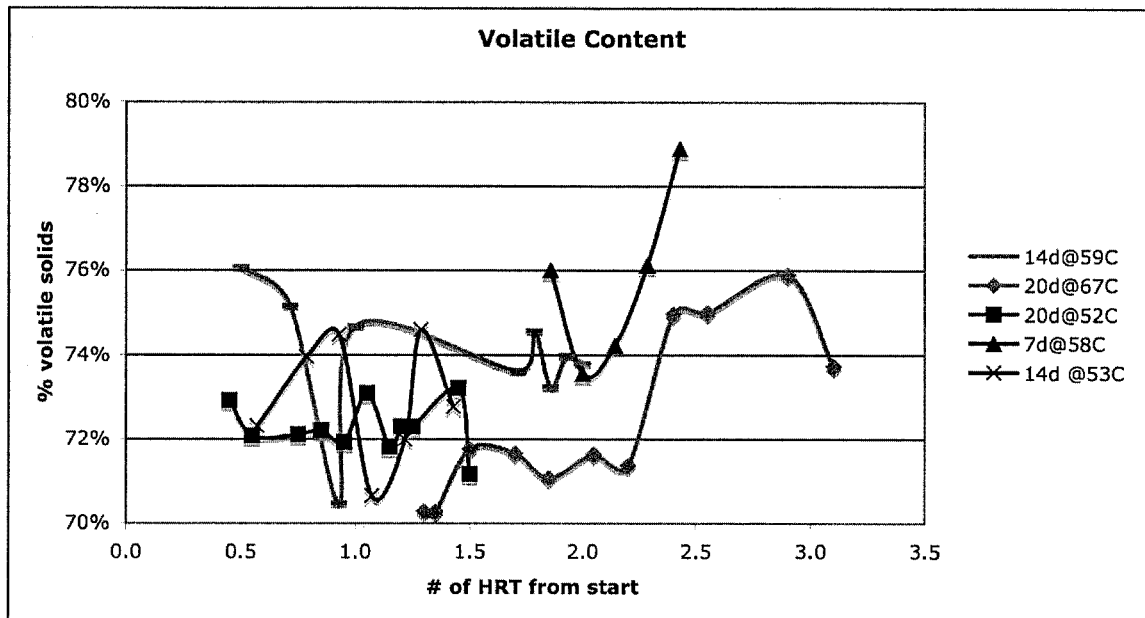


Figure 3: Percentage Volatile Solids Content in ATAD 2 over HRT

Figure 4 shows the change in volatile solids reduction as the reactor stabilized. From Figure 4, it is clear that the solids destruction is a better measure of the stability of the reactor than percentage volatile solids content, as the results are less sporadic. However, for the condition 20d@67C, it took the reactor more than 2 HRT to stabilize, but for 20d@52C, it took less than 1 HRT. This shows that stability is dependent on more than simply the number of retention times that have elapsed. This plot also shows that, occasionally, even two retention times is not sufficient for stabilization; this is clear for 7d@58C in particular. However, under most circumstances, two HRT was found to be sufficient to achieve quasi-stability. Other important factors for stability are consistent operation including aeration and temperature.

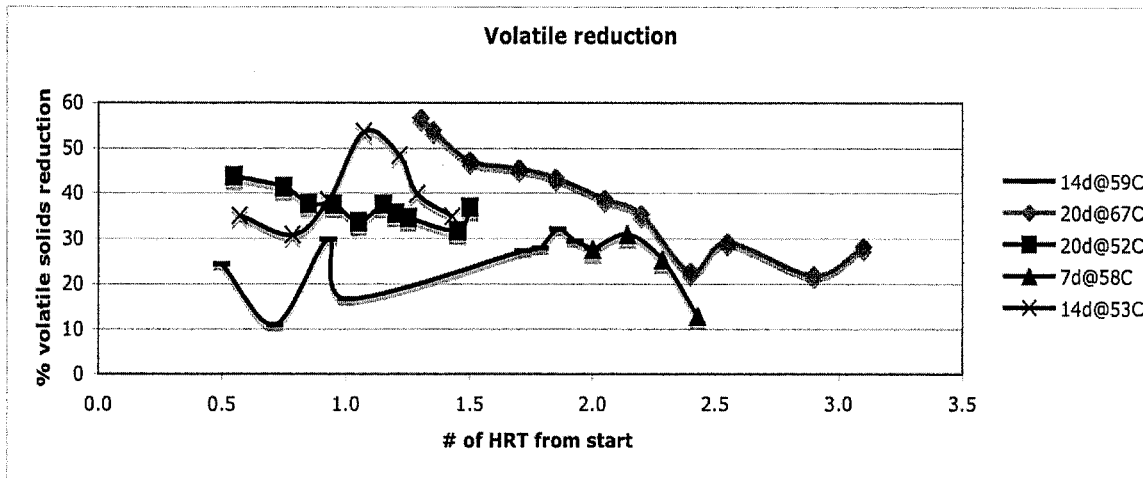


Figure 4: Volatile solids reduction in ATAD 2 for each condition

Another method of measuring stability is SOUR. However, this is complicated by the need to account for the temperature at which the test was done. Figure 5 shows the corrected SOUR values based on Total Solids (TS) and how they changed as the reactor approached stability. It is easy to determine when stability has been achieved for some of the conditions (i.e. 20d@67C) but not for others (20d@52C). Below 1.5 mg oxygen/h/g solids is often understood to mean moderately stable, and below 1.0 mg/h/g is considered stable.

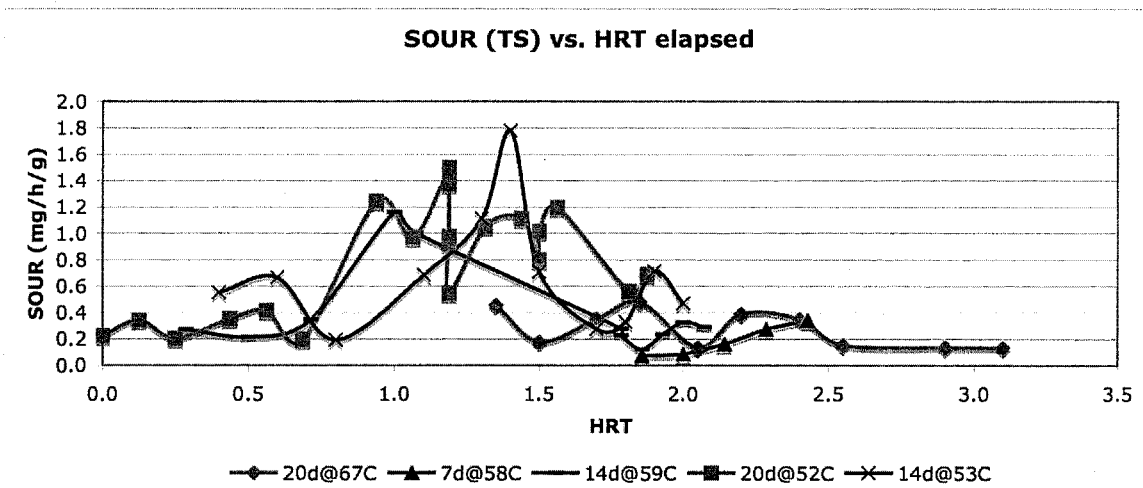


Figure 5: Stability monitored using SOUR values based on Total Solids

3.4 Analytical Methods

All analysis was done on site at the Salmon Arm WPCC except for the proximate analysis of crude sludge, waste activated sludge, and ATAD 2 contents.

3.4.1 Solids

Since the most common measure of stability of biosolids is based on solids destruction, particularly volatile solids destruction, this was considered one of the most important parameters to be monitored. Total and volatile solids content of the crude sludge, waste activated sludge (WAS), and test reactor contents was done, not only on the designated testing days but also every second or third day, from start up of several of the conditions, in order to determine if the test reactor had achieved stability.

Total and Volatile Solids content were measured as described in *Standard Methods for the Examination of Water and Wastewater* Method 2540. Moisture content was obtained by heating a small sample (<25mL) to 100 – 130°C in a moisture analyzer until the weight stabilized, which took between 60 and 90 minutes depending on the sample. The samples were allowed to cool in a desiccator and then weighed. The samples were then re-dried for a minimum of fifteen minutes in another oven at approximately 100°C, cooled and weighed. This drying, cooling and weighing was repeated until successive measurements were within 0.5 mg.

After the dry weight was obtained, the samples were fired in a muffle furnace that was heated to 500+/- 50°C for a minimum of fifteen minutes. The samples were then allowed to cool in a desiccator and weighed every five minutes, until two consecutive measurements were the same.

3.4.2 SOUR

Although all of the combinations of temperature and HRT to be tested have been proven to produce stable biosolids, it was still considered important to monitor a few parameters that would demonstrate the acceptability of the process. Since SOUR is used as a measure of stability, it was considered an important parameter to monitor. SOUR

was measured on the testing days but was also measured from start up of many of the conditions, in order to determine if the test reactor had achieved stability. Because the oxygen uptake rate of a sample is affected by the amount of time it is exposed to the atmosphere, SOUR tests were always done immediately after the sample was taken. SOUR tests generally followed the procedure described in *Standard Methods*: Method 2710B; however some changes had to be made to adapt the test to the material being analyzed.

The tests were carried out in a modified vacuum flask. Instead of providing a vacuum as suggested in *Standard Methods*, tubing was attached to the side port and the other end immersed in water to provide an exhaust vent for the air being pumped into the sample. The sample was aerated using a fish tank air pump and by mixing with a large stirring bar. The dissolved oxygen in the sample was measured using a YSI probe, which is able to accurately and quickly measure very low amounts of dissolved oxygen on an analogue scale. The sample was aerated until there was a minimum of 4ppm of dissolved oxygen. However, sometimes the sample had such high oxygen demand that this was difficult to achieve. In these cases, the samples were allowed to cool to 25°C before the test was carried out, as the SOUR can change significantly with temperature. Once the desired dissolved oxygen concentration was reached, the pump was shut off and mixing stopped or reduced to a minimum. Dissolved oxygen readings were taken every 0.1ppm or as quickly as possible for a minimum of five minutes. The dissolved oxygen concentrations and times were plotted and the slope of the line was taken as the OUR. The SOUR is determined by dividing the OUR values by total or volatile solids content and converting to the proper units.

OUR values are significantly affected by temperature and have to be corrected to an equivalent at 20°C. This correction is done using the Van't Hoff Arrhenius equation.

$$\text{SOUR}_T = \text{SOUR}_{20} \theta^{T-20} \quad (\text{Eq. 2})$$

Typical theta values for oxygen consuming processes are between 1.03 and 1.056 for $T > 20$ and from 1.08 to 1.135 for $T < 20$. *Chemistry for Environmental Eng.* 3rd

Ed. suggests 1.056 from 20-30°C and 1.135 for 5-18°C. The textbook *Biological Waste Treatment* by Grady et al. (1999) suggests 1.03 for 20-35°C and 1.08 for 10-20°C.

However, because the data seemed so dependent on the SOUR value, several attempts were made to determine a θ for this process. To determine theta, an oxygen uptake rate test was done on the same sample at several different temperatures. These rates were then divided by the rate at 20°C and plotted against the test temperature less 20°C. The temperature tests were carried out on three different days, and the results are presented in Figure 6. The theta was calculated using the following relationships.

$$\text{SOUR}_T = \text{SOUR}_{20} \theta^{T-20}$$

$$\frac{\text{SOUR}_T}{\text{SOUR}_{20}} = \theta^{T-20}$$

$$\ln\left(\frac{\text{SOUR}_T}{\text{SOUR}_{20}}\right) = (T-20) * \ln(\theta)$$

$$\theta = \exp\left(\frac{\ln\left(\frac{\text{SOUR}_T}{\text{SOUR}_{20}}\right)}{T-20}\right)$$

Figure 6 presents $\ln(\text{SOUR}_T/\text{SOUR}_{20})$ on the y-axis and $(T-20)$ on the x-axis, so that the slope of these lines can be used to find theta values. However, only the smallest slope produces a theta value that is reasonable and close to values already published; thus the value used was $\theta=1.110$. It is unclear why the larger slopes were produced.

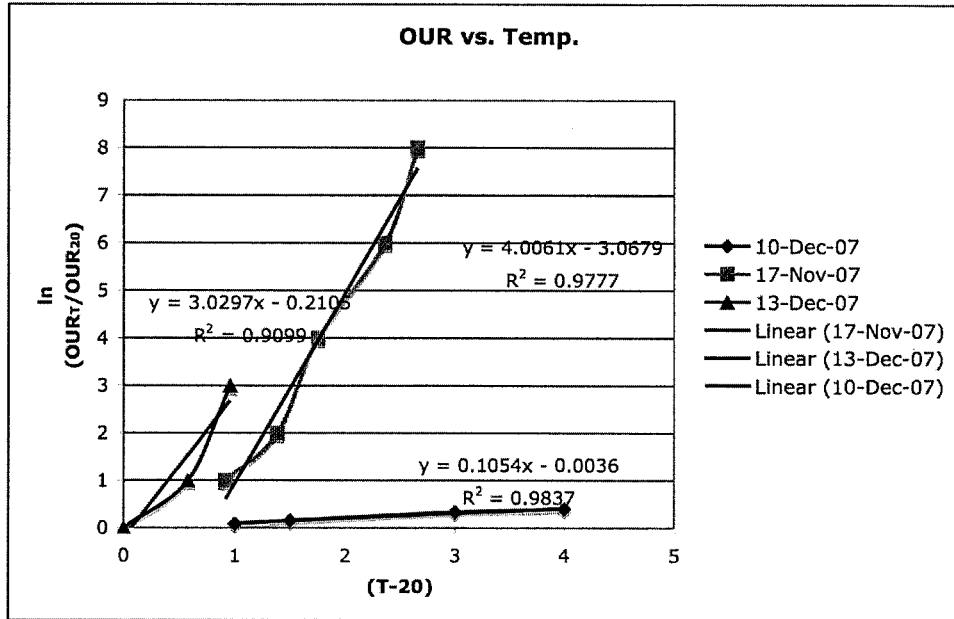


Figure 6: Plot for Determining Temperature Coefficient

3.4.3 Ammonia

Since one of the key odorous gases produced by ATAD reactors is ammonia gas, the concentration of ammonia in solution was monitored so that it could be correlated with the concentration of ammonia gas. Ammonia is also a weak base that provides some of the alkalinity that is present in an ATAD reactor. The amount of ammonia that is in solution is highly dependent upon pH such that, at high pHs, more ammonia than ammonium is present. Since ammonia is easily transferred into the gas phase, high pHs or high temperatures often lead to “stripping” of ammonia as it is released. The amount of ammonia released can also be a function of temperature, as a greater amount of energy is available and allows the ammonia to move into the gaseous state. The typical relationship between dissolved ammonium and gaseous ammonia is described with an S-shaped curve (not included for copyright reasons) where below a pH of 7 only dissolved ammonium exists and above a pH of 11 only gaseous ammonia exists. At a pH of 9.25 there is equilibrium between the gaseous and dissolved phase at room temperature (25°C) (Tchobanoglous et al., 2003). This curve also is influenced by temperature and shifts to

the left as temperatures increase above room temperature so that at lower pH there is more ammonia gas.

Ammonia concentration in ATAD 2 was measured by diluting the samples 1:1000 and using an electrometer as described in *Standard Methods*: Method 4500-NH₃ F.

3.4.4 pH

A healthy ATAD reactor will operate a little above neutral on the pH range, likely between 7 and 9. Therefore, pH was monitored because it is an important parameter that indicates the health of the reactor.

pH was measured using a pH meter as described in *Standard Methods*: Method 4500-H⁺ B. Because pH is related to temperature, pH measurements were not recorded until the sample had stabilized near room temperature.

3.4.5 Alkalinity

Alkalinity is an important parameter and was monitored because of its link to ammonia, proteins, and biological activity in the reactor. The ammonia in solution offers buffering capacity and is thought to originate from the deamination of proteins which leaves a carbohydrate structure that is more bio-available.

Alkalinity was determined using the titration method as described in *Standard Methods*: Method 2320 B. The standard acid used was 0.02N sulphuric and titrations were done to a pH of 4.5.

3.4.6 Proximate Analysis

Proximate analysis was undertaken in order to give a description of the sludge being digested. Since the three major classes of macronutrients are carbohydrates, proteins, and fats, monitoring the amount of these in the sludge can give a sense of the character of the sludge and a better understanding of the digestion process. Knowing the protein, carbohydrate, and fat content of the sludge also allows it to be compared with other sludge. Since ammonia gas and amines are thought to be by-products of the

breakdown of protein, the protein content of the sludge is of particular interest in this study.

Carbohydrates are some of the most basic elements of food and most important sources of energy. Carbohydrates include simple sugars such as glucose and larger, more complicated structures such as cellulose. Energy from the sun is stored in plants through carbon bonds, which, with the addition of hydrogen and oxygen in specific arrangements, form the basis of carbohydrates. Carbohydrates can be as simple as $(\text{CH}_2\text{O})_n$ where n is an integer between three and eight. Glucose and sucrose (glucose linked to fructose) account for a large part of the solid content of fruits and vegetables.

Fats and lipids are a large source of energy in the human diet, approximately 34% (Mahen and Scott-Stump, 2004). Our ability to store fat is what allows us to go without food for long periods of time. Fat also acts as insulation for humans and facilitates the digestive process. Lipids are small molecules from plant and animal tissue. Dairy fat is usually smaller than animal fat with only four to six carbons in a fatty acid chain, versus sixteen to twenty. A fatty acid chain is a chain of carbon and hydrogen atoms bonded to a structure such as glycerol, which is composed of hydrogen, carbon, and oxygen.

Proteins are complicated compounds containing nitrogen and made up of amino acids and chemical bonds. Of the macronutrients, proteins are the only ones that normally contain any form of sulphur. Plants form amino acids and proteins by “fixing” inorganic nitrogen from the air or soil. Amino acids are organic compounds “containing an amino group (NH_2) and a carboxyl group (COOH)” (Mahen and Scott-Stump, 2004). Although plant structures are mainly made of carbohydrates, human and animal bodies are built on proteins. Proteins can also act as a source of energy if the nitrogen is removed, resulting in a carbohydrate. There are twenty amino acids required by humans; of these twenty, only three contain sulphur in them. However, the amino acids containing sulphur are found in cheese, eggs, milk, meat, cereal, legumes, nuts, seed oils, soybeans, and yeast.

A healthy liver “deaminates” amino acids into carbohydrates and little or no protein is excreted, only nitrogen is excreted in the urea. A high level of protein in the urine can be an indication of glomerular disease or other conditions that affect kidney function. Therefore, high levels of protein in wastewater are not likely from human sources.

Samples were taken for proximate analysis once the reactor had stabilized and on testing days. Samples of fifty to one hundred mL were taken, frozen, and shipped to CanTest laboratories in Vancouver, for proximate analysis to be completed. Samples were taken of crude sludge, TFAS, and test reactor contents, in order to be able to compare them and distinguish which components had been degraded. Although proximate analysis includes moisture, ash, carbohydrate, protein, fat, and energy content, only carbohydrate, protein, and fat content were relevant to this study.

The CANTEST Laboratories analyses were undertaken in accordance with “Official Methods of Analysis of the Association of Official Analytical Chemists” (2003).

3.4.7 ORP

Oxidation Reduction Potential is an important parameter for judging the state of the reactor as it indicates how aerobic or anaerobic the process is at any time. This can give an indication of the odours that can be expected from the process, as anaerobic conditions typically produce more odorous compounds than aerobic conditions. It also is related to pH, as ORP decreases with an increase in pH (Kelly, 1990).

ORP was measured using a Ag/AgCl₂ ORP probe immersed in the reactor. Readings were taken approximately every three seconds.

3.4.8 Gases

The gases monitored were hydrogen sulphide, methyl mercaptan, ammonia, amines, and dimethyl sulphide, as these were found to be the odorous gases with the

highest concentration in the only other published study done on ATAD Odours (Bowker and Trueblood, 2002).

Gas concentrations were measured using a colourimetric method. Although *Standard Methods* recommends the Gas Chromatographic Method, this is not possible in the field and it would be difficult and expensive to have samples shipped to a lab frequently. Gas Chromatography may be more accurate for measuring these compounds; however, it is expensive, cannot be done in the field, and often the compounds of concern, particularly amines, adhere to solids surfaces and would be likely to adhere to the inside of a GC column. This was confirmed when two gas samples were taken and analyzed using a gas chromatograph and none of the expected compounds were found. This is likely due to the gases adhering to the sample container or the GC column.

Standard Methods also suggests a volumetric method of measuring gases; however, this is only appropriate for the main gases produced in an anaerobic digester, which did not include all of the gases measured in the study. Instead, GasTec Detector tubes were used that change colour to indicate the concentration of the gas being measured.

To measure dimethyl sulphide, an extra piece of equipment was required, called a pyrolizer, which is thought to heat up the sample and remove moisture. The pyrolizer was attached to the end of the pump and the tubes were connected to it.

Although gas concentrations can vary throughout the day with the semi-continuous feeding procedure used, monitoring of the gases of concern was always done at approximately the same time of day, typically between 1 and 4pm, several hours after the daily transfer was completed (to ensure consistency of results).

Since the tubes were only accurate up to 90% humidity and 40°C, there was some initial concern that the humidity and temperature in the reactor would be too high. So, initially the air was pumped, using a peristaltic pump into a glass vessel containing ice and then into a Tedlar bag. However, this system did not work very well and the gases often could not be measured after they had passed through this system. It was also

discovered that, although the humidity was high in the reactors it was rarely higher than 90% and although the temperature of the liquid was almost always higher than 40°C, the air in the headspace was not. Hereafter, the GasTec pump and tubes were inserted directly into the headspace of the reactor and measurements were taken directly. The temperature of the headspace was also measured in order to apply the appropriate correction factor to the measurement.

4 Results and Discussion

All testing was done in the summer and fall of 2007. The first condition was set up and tested in August 2007. Because of the time requirements for set-up and stabilization of the reactor, one condition was tested per month for the rest of the calendar year.

Since five conditions were tested and the same parameters measured for all conditions, most results will be presented in box and whisker diagrams. These diagrams are a visual way of presenting the results and displaying whether the results under one condition were statistically different from those of another condition. A Box and Whisker Diagram shows the median value of a set of measurements, the maximum and minimum value measured and the first and third quartile of the measurements. The first quartile of a set of measurements is the value below which lies a quarter of the values measured. The third quartile is the value above which lies a quarter of the values. The “box” goes from the first quartile to the third quartile and the whiskers extend to the maximum and minimum values measured. A marker inside the box denotes the median.

One statistical method for analyzing, numerically, the results of the data is to perform an Analysis of Variance (ANOVA). This type of analysis is used to look for differences between groups. It accomplishes this by comparing the means and variances of several groups of measurements of the same parameter. It is similar to a t-test but is more complicated as it is used to compare more than two groups. For this study, these groups are the various combinations of Hydraulic Retention Time (HRT) and temperature that were tested. These groups must be independent, and for this case, they likely are. There is some dependency between results because the test reactor could not be drained completely between condition sets; however, this is very small. An ANOVA tests the null hypothesis, that the means are not significantly different. If the hypothesis is true, the critical value of F at (say) 95% confidence level ($\alpha = 0.05$) should be larger than F. All results reported here are based on a 95% confidence level.

The null hypothesis (that there is no significant difference between groups of results) when it occurs, is a result of the fact that, in most cases, the variance in measurements is too high, or simply because this parameter is not affected by the changes in HRT and temperature that were made.

4.1 Standard Liquid Parameters

4.1.1 Specific Oxygen Uptake Rate (SOUR)

Although SOUR was used to determine if, and when, the reactor had achieved stability, it was also monitored after quasi-stability was achieved, in order to see if different conditions produced more stable or less stable sludge.

However, SOUR values are very temperature dependent and so a temperature correction coefficient must be used. To determine the coefficient, the Oxygen Uptake Rate (OUR) of a sample was measured at different temperatures. This experiment was done three times, on three different days. A temperature coefficient (θ) of 1.110 was decided upon, as this seemed the most reasonable of the three calculated θ values and agreed with values reported in the literature for other biological treatment systems.

Some measures of stability use a SOUR value based on Total Solids (OUR/TS), while some use a SOUR based on Volatile Solids. The Water Environment Research Foundation's assigns meanings to ranges of VS-based SOUR values as reported in *Defining Biosolids Stability: A Basis for Public and Regulatory Acceptance*, and as shown in Table 2.

Table 2: Respiration Rates and Meanings

Respiration rate (mg O ₂ / g VS / h)	Rating
0 – 0.5	Very Stable
0.5 – 1.0	Stable
1.0 - 1.5	Moderately Stable
>1.5	Unstable

Figures 7 and 8 show the range of SOUR values obtained for each condition set tested. Both of these plots are very similar visually, with a difference only in the values obtained. The similarity is caused by the way in which SOUR values are obtained (by dividing the OUR by the percentage of volatile or total solids). Performing an ANOVA on the values presented in Figure 7 yields an F value of 18.1 and an F-critical of 2.8 (significant difference). The F value for the results presented in Figure 8 is 17.7 and the F-critical is 2.8 ($\alpha = 0.05$), which means the results are also significantly different. It is clear from these values and from the diagrams that SOUR values obtained for 20d@52C are significantly different from that of the other conditions.

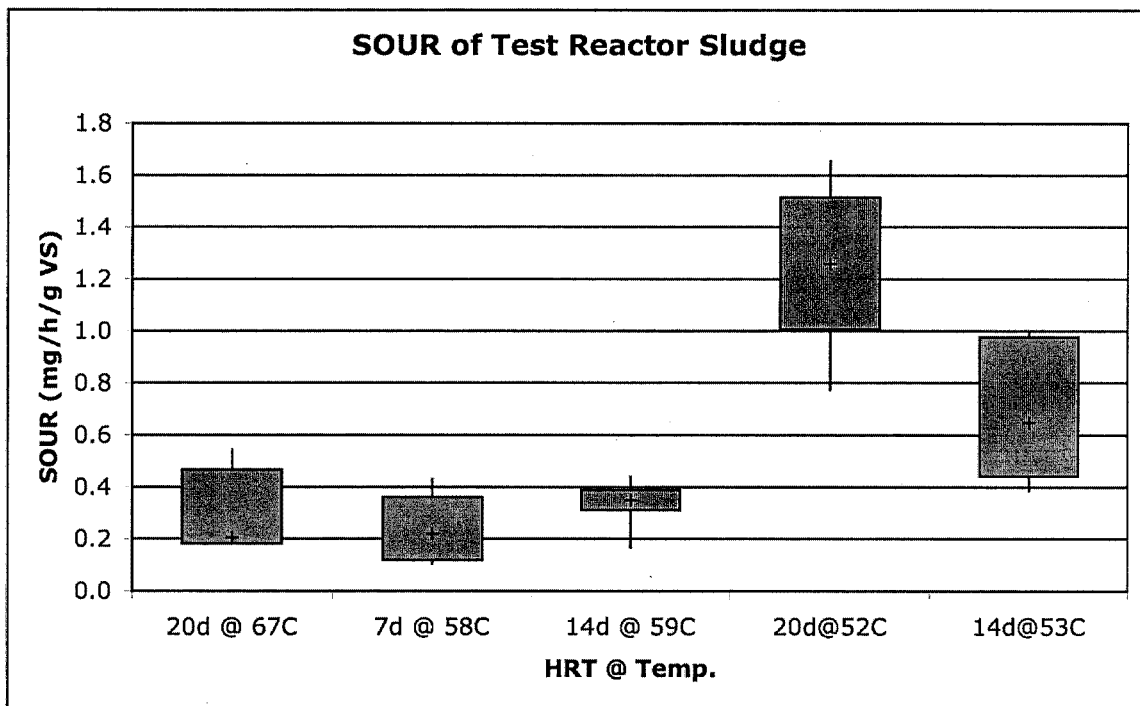


Figure 7: Box & Whisker Diagram of VS-based SOUR values

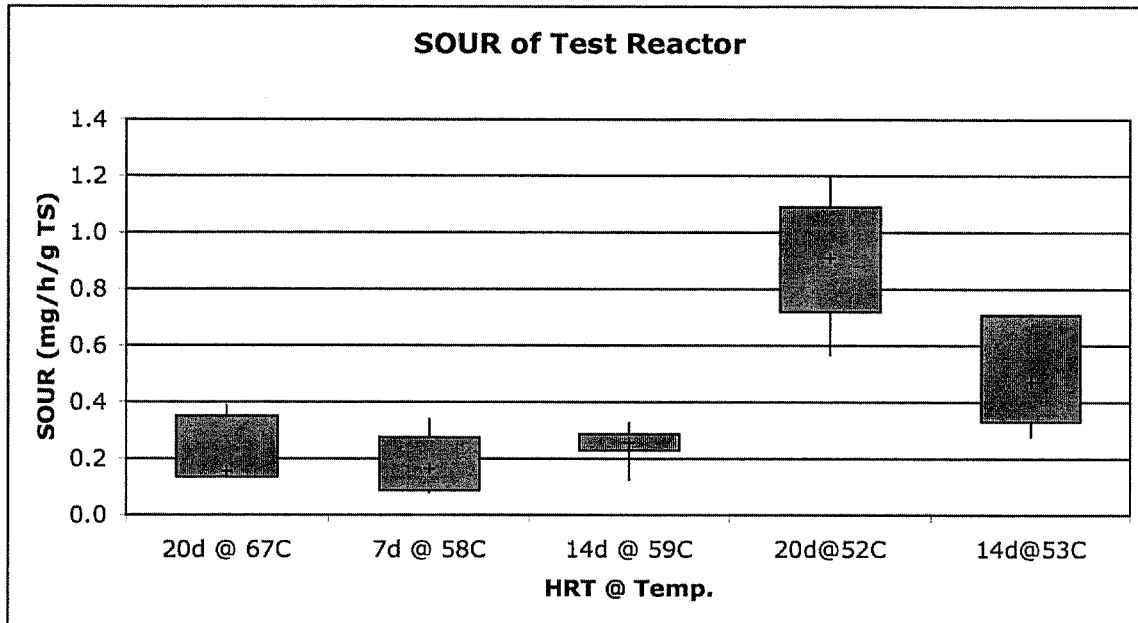


Figure 8: Box and Whisker Diagram of SOUR values based on TS

By performing an ANOVA on the first three groups and the last group of either set of results we obtained an F value of 5.7 and F-critical of 3.2, based on the VS SOUR values. This shows that the SOUR results from 14d@53C are also significantly different than SOUR values from the first three experiments. This can be confirmed by doing another ANOVA on only the first three experiments, resulting in an F value of 0.56 and an F-critical of 3.8. The same result is found when the ANOVA is done on the SOUR values based on TS. The F value found in this case, for the first three experiments only, is 0.43 and the F-critical is 3.8 again. This seems to indicate that SOUR values are lower, and hence the sludge is more stable at higher temperatures. This can be confirmed by performing an ANOVA on the results from 14d@59C and 14d@53C. When this is performed for both the VS and TS results, the F-critical value is 5.1 and an F value is 8.1 ($F > F\text{-crit}$); thus, they are indeed significantly different.

4.1.2 Volatile Solids Reduction

The percentage of volatile solids reduction normally anticipated from a sludge digestion processes is about 40%. The percent reduction values were determined by comparing the percentage of volatile solids (VS) in the crude and trickling filter activated

sludge (TFAS) with that of the test reactor. The %VS in the crude and TFAS were combined to determine the VS in the feed using the % of each fed to the ATAD system each day. Each day's measurement of VS in ATAD 2 was compared with the average VS of all the feed for one HRT prior to that day. This was considered the best way to account for the variations in feed and the changes in the sludge over time.

Figure 9 shows the median and variance in the Volatile Solids Reduction for each condition. An ANOVA of these results yields an F value of 8.2 and an F-critical of 2.9; therefore the VS reductions are significantly different. Doing another ANOVA on only the first four conditions shows that these are also significantly different (F=4.4 and F-critical = 3.3). Performing a third ANOVA on the first three conditions only, yields an F value of 1.3 and an F-critical of 4.0, indicating that these are not significantly different. This is a similar result to what was found for SOUR values. The results tend to be lower for higher temperatures.

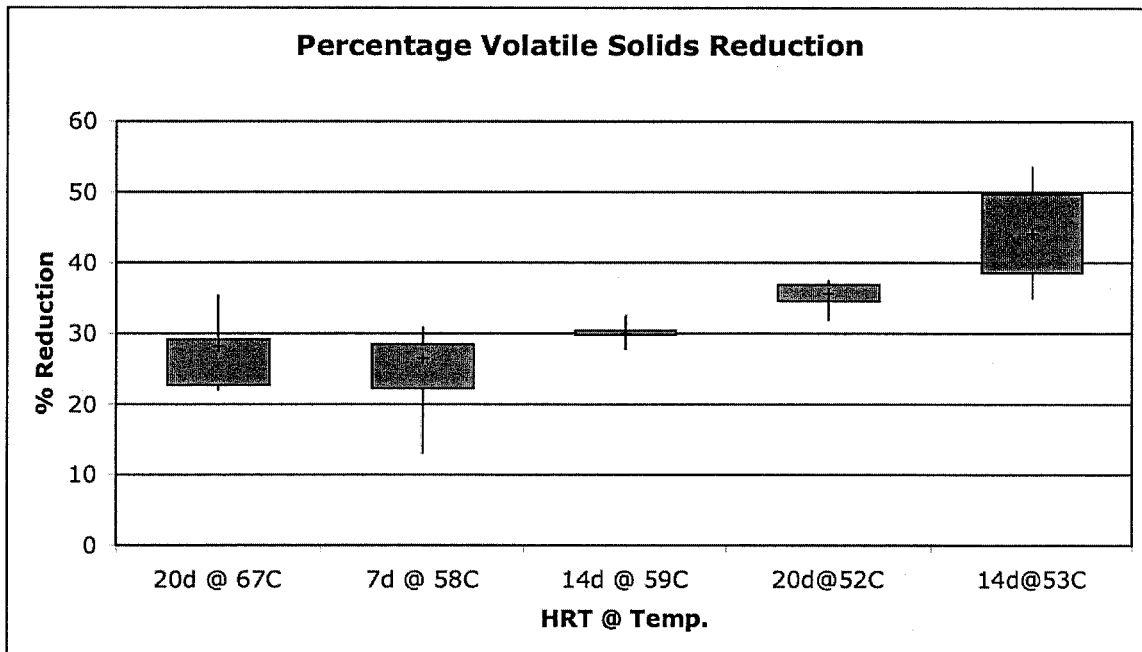


Figure 9: Box and Whisker Diagram of Percentage Volatile Solids Reduction

Visually, it is also clear that the VS reductions for conditions with the same overall HRT are also different. It appears temperature has more of an effect than HRT

does (compare 14d@53C with 14d @59C and 20d@52C with 20d@67C). For the two groups with an HRT of 20d, the F value is 8.7 and F-critical is 5.3; for 14d the F value is 13.7 and F-critical is 5.6 (they are both significantly different).

4.1.3 Total Solids Reduction

Total solids reduction was also monitored in the reactors. Figure 10 shows the Total Solids reduction for each set of conditions tested. The results are significantly different ($F=12.1$ and $F\text{-critical}$ is 2.9) and from the diagram, it seems that an HRT of 14 days results in higher solids destruction than at 20 days. However, when an ANOVA is done comparing only the 14d and 20d HRT data (last four groups) the results are not significantly different ($F\text{-crit}>F$).

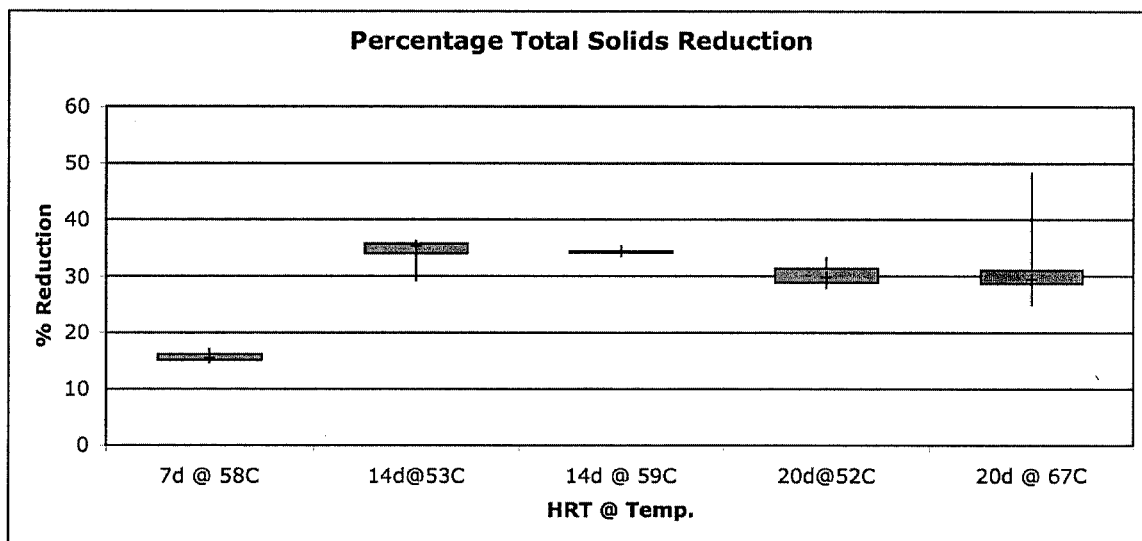


Figure 10: Box and Whisker Diagram of Total Solids Destruction

An ANOVA performed on the results of the two tests done at an HRT of 14d shows that the results are not significantly different ($F=0.09$ and $F\text{-crit}=5.3$). Similarly, an ANOVA was done on the groups with an HRT of 20d and yielded an F of 0.28 and F-critical of 5.3; this also shows that these results are not significantly different. It is clear that Temperature does not make a significant difference and HRT is the governing factor in total solids destruction.

4.1.4 Ammonia

Figure 11 shows the median and variation in the ammonia concentration of the liquid in the test reactor, for each condition. Performing an ANOVA on the results shows that the results are not statistically different from one another ($F\text{-crit} > F$). The ammonia concentration in the liquid seemed to remain around 1200 mg/L and did not seem to be affected by temperature or HRT. An ANOVA done on conditions 4 & 5 (same temperature) and 1 & 4 (same HRT) both have an $F\text{-crit} > F$, confirming that neither temperature nor HRT make a significant difference.

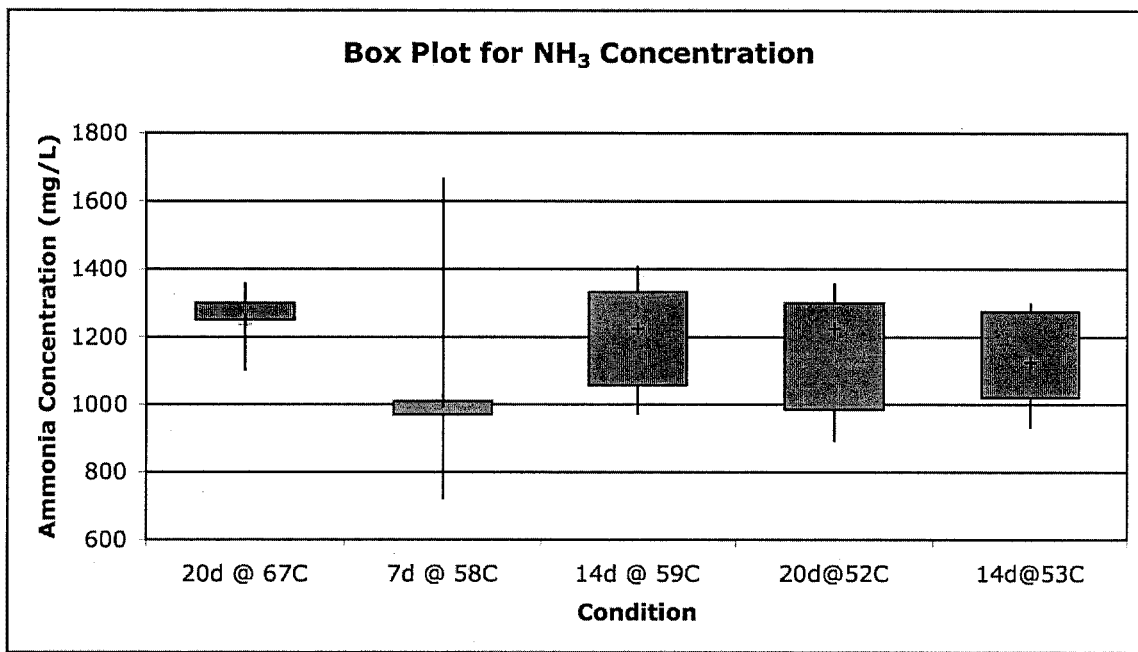


Figure 11: Box and Whisker Diagram of Ammonia Concentrations in test Reactor

4.1.5 Alkalinity

The median alkalinity and variation are shown below in Figure 12. An ANOVA performed on the data shows that the results are, in fact, statistically different ($F=45$ and $F\text{-crit}=2.8$). However, an ANOVA done on the last four conditions shows that these are statistically the same ($F\text{-crit} > F$). This trend of higher results in the first group than for the other four groups is repeated in the pH results indicating that these results are related.

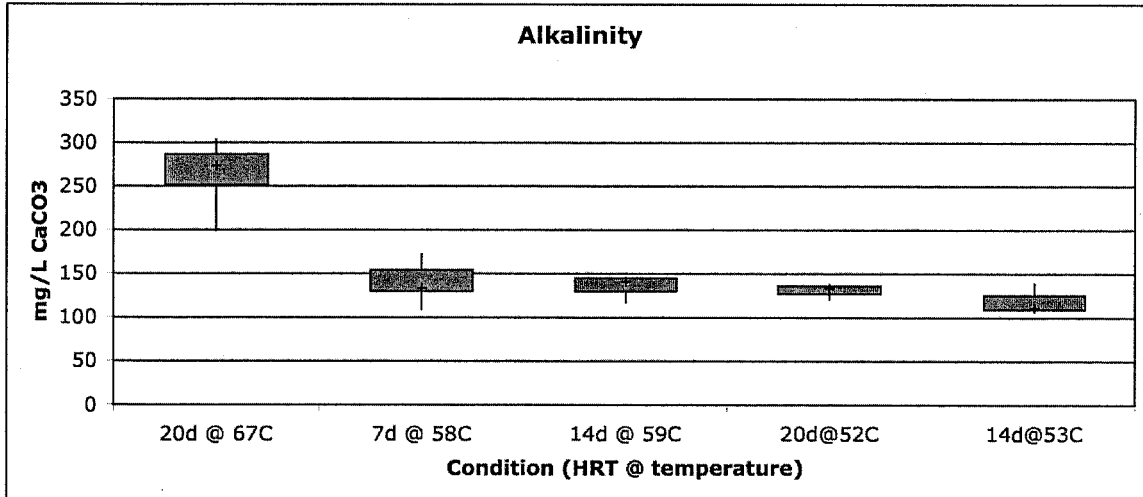


Figure 12: Box and Whisker Diagram of Alkalinity for each Condition

Interestingly, an ANOVA completed on only the two groups with an HRT of 14d, shows these results are significantly different ($F\text{-crit}=5.0$ and $F=5.8$, $\alpha = 0.05$). This indicates that the alkalinity is higher for higher temperatures. This might be expected, as more protein is degraded at higher temperatures to ammonia, and ammonia is a form of alkalinity. However, this change was not evident from the actual ammonia results, indicating that other forms of alkalinity are contributing to these increases. It also cannot be CO_2 that is contributing to the alkalinity at higher temperatures as the solubility of CO_2 decreases with increasing temperatures. However, hydrogen sulphide could be the source as it does follow the pattern of increased solubility with increased temperature.

One might expect (because the results of the first condition with an HRT of 20d are higher) that HRT also has an effect on alkalinity. However, when the results from 20d@52C are compared with 14d@53C (almost the same overall temperature), they are not significantly different ($F\text{-crit}>F$).

4.1.6 pH

The range of pH values encountered for each condition is presented in Figure 13. From the diagram, it is clear that the pH values for the first condition were higher than the rest. Performing an ANOVA on the data confirms this, $F\text{-crit} < F$ for all five, but $F\text{-crit} > F$ for the last four, showing that these four are not significantly different. However,

an analysis of the groups with an HRT of 14d does not yield the same result found with alkalinity. pH is not affected by these changes in temperature ($F\text{-crit} > F$), perhaps the first group can be explained by the large jump in temperature that is observed. The higher result for the first condition cannot be explained by the HRT; when comparing 20d@52C with 14d@53C the critical F values is greater than F showing that they are not significantly different. The increased pH at the higher temperature could be explained by the presence of CO_2 , which is less soluble at increasing temperatures. As it leaves the liquid the acidity is reduced, increasing the pH.

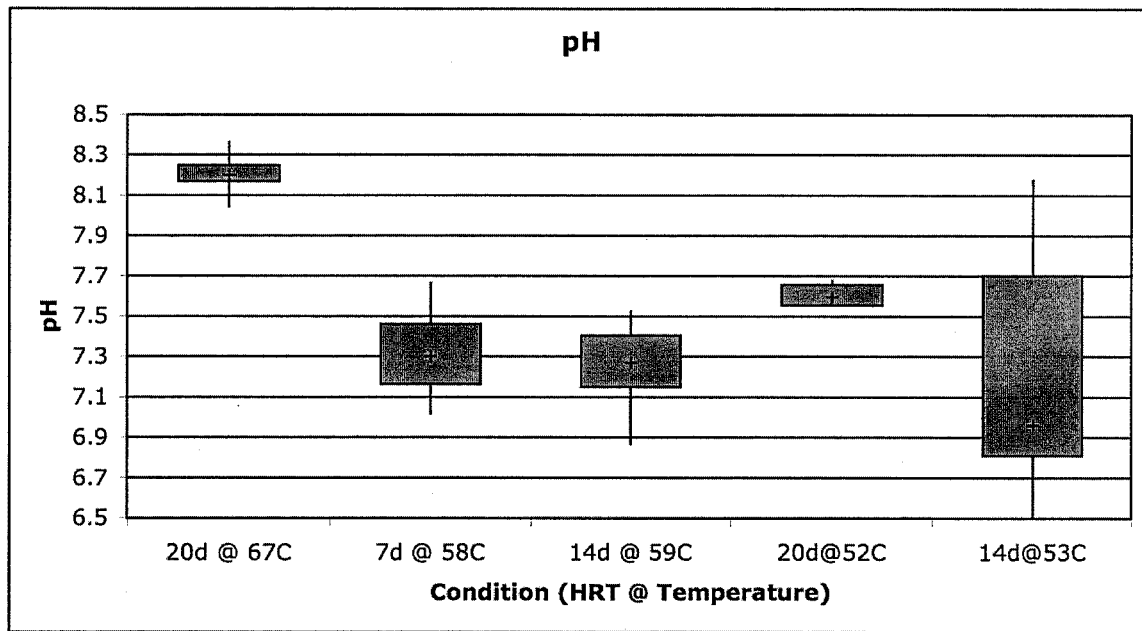


Figure 13: Box and Whisker Diagram of pH Values

4.1.7 ORP

ORP results obtained from this study were obtained every hour on the half hour and were all below -400mV. This is low for an ATAD system, most of which operate between 0 and -350mV. Although the aeration was varied for each condition and often throughout each day, temperature is concluded to respond much more quickly to changes in air supply, than does ORP. It is thought that, in order to raise the ORP, a much greater volume of air would be needed, which would likely cause the temperatures to drop significantly.

Figure 14 summarizes the ORP data obtained for the test reactor during the study. Performing an ANOVA on the data shows that the results are significantly different ($F=130$ and $F\text{-crit}=2.6$). The results are presented in order of the conditions tested and there seems to be a downward trend, excluding the last group.

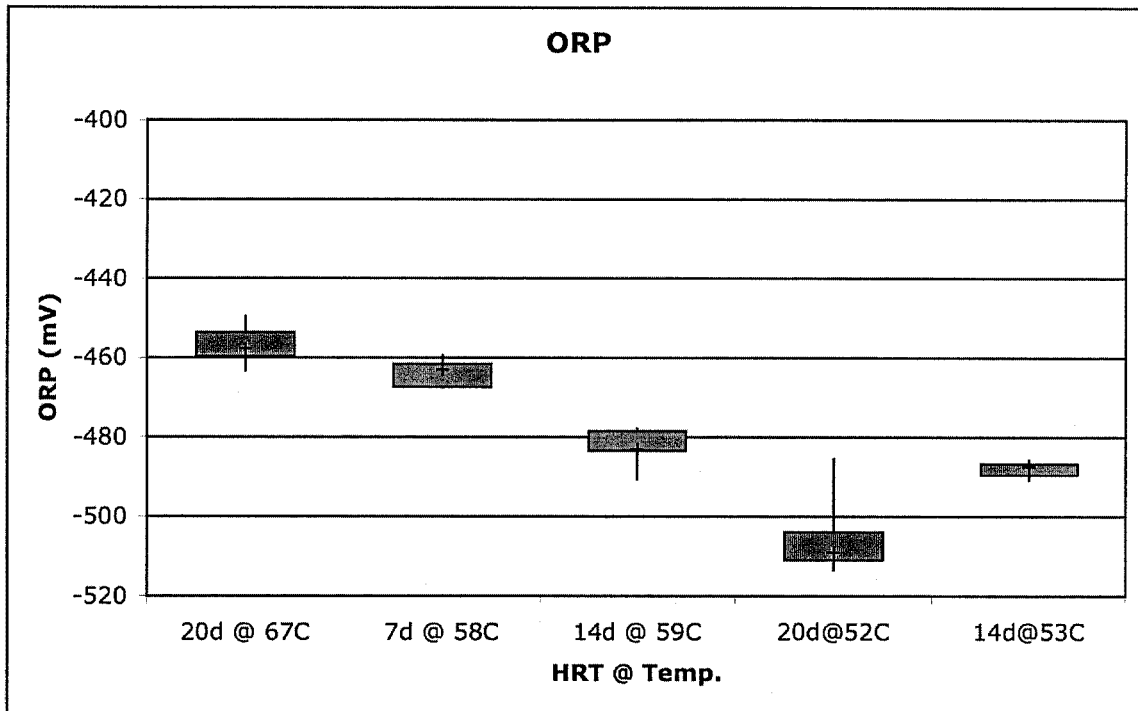


Figure 14: Box and Whisker Diagram of ORP values

It is clear from the figure that there is no trend based on HRT. It appears that there could be a trend, based on temperature; however, when group 14d@59C is compared with group 14d@53C there is no significant difference ($F_{crit}=5.3$ and $F=4.3$). Therefore, ORP is not significantly affected by changes in HRT or Temperature. ORP measurements are fairly dependent on the particular probe used, this might explain some of the variability.

4.1.8 Discussion

SOUR values were lower, indicating more stable sludge, when the test reactor was operated at higher temperatures. Thus, higher temperatures seem to mean a more stable process. The SOUR results are somewhat questionable at such high operating temperatures, as the sludge has to cool down drastically for the test to be carried out.

However, since the testing method was fairly consistent throughout the study, the results should still be comparable to each other.

Volatile solids reduction has the same overall trend as SOUR, with higher temperatures leading to lower values. Whereas, for SOUR values, where this was obviously a positive thing, this is not the desired outcome for solids reduction; the purpose of a sludge digestion system is to destroy solids. However, there are several potential reasons for this. Firstly, the percentage of volatile solids in the feed changes significantly depending on the state of the process and what ratio of crude to TFAS is used. For example although 14d@53C produced a greater overall volatile solids reduction than did 14d@59C the percentage of volatile solids in the feed was higher for the lower temperature condition so that more reduction was achieved even though the percentage of volatile solids in the product was the same. Another possible explanation is that at the higher temperatures the biological activity is somehow restricted. This is less likely as the SOUR results are also lower for higher temperatures indicating that the bacteria are clearly active. It is also possible that the fixed solids are somehow not as conservative at the higher temperatures and the ratio of fixed to volatile solids is affected. Volatile solids reduction is a good indicator of stability; however, the amount of reduction achieved was consistently less than expected for the given time and temperature combinations. The combinations of HRT and Temperature that were used were all within the ranges used at other plants to meet the regulations. Therefore, instead of a specific amount of volatile destruction being regulated, perhaps consistently achieving the same amount would be more meaningful.

In terms of total solids destruction, temperature does not have the effect it does with VS destruction. HRT is the key parameter in terms of total solids destruction.

Alkalinity is generally higher for higher temperatures, likely due to dissolved H₂S, and is also affected by pH. Ammonia and pH are not clearly affected by changes in HRT or temperature. However, the first condition produced both high pH and high alkalinity. The high pH could be due to CO₂ leaving solution. One would expect that the breakdown of protein to ammonia might cause higher alkalinity; however, there is no indication of this in the ammonia results.

ORP is also not affected by changes in HRT or Temperature. The low ORP values observed in this study are a result of the aeration regimes used to achieve the high temperatures. The large variations could be partially due to the probe used.

4.2 Protein, Carbohydrate and Fat Content

4.2.1 Protein

The protein content of sludge is an important parameter because of its links to odour production. Different odours are produced during the breakdown of proteins than are produced during the breakdown of carbohydrates or fats. Also, as protein is degraded, more ammonia can be formed, sometimes affecting alkalinity. There is also suspected to be a build up of protein in ATAD systems because of preferential breakdown of carbohydrates and fats. Figure 15 shows the protein content of the sludge in grams per 100 grams of sludge.

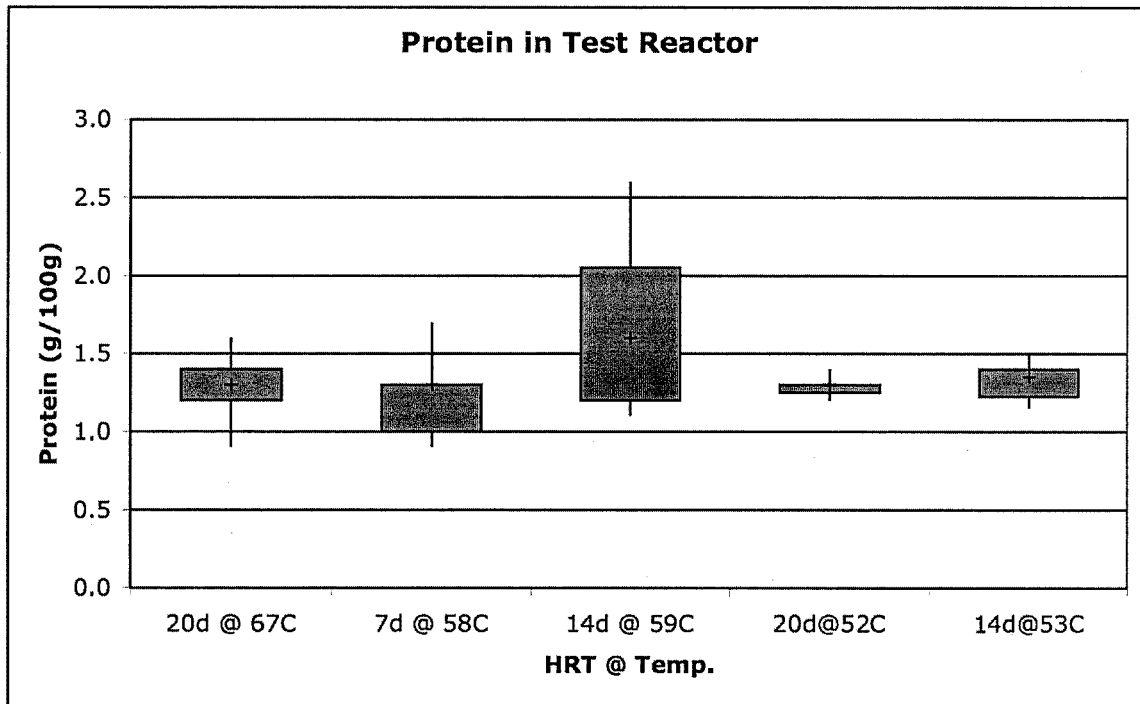


Figure 15: Protein Content in Test Reactor

Performing an ANOVA on the data demonstrates that there is no significant difference resulting from these changes in temperature and HRT (F-crit=2.8 and F=2.1).

Figure 16 shows the average protein content of the various type of sludge. The input sludge is a weighted average of the protein content in the crude and TFAS based on

the amount of each that was fed to the ATAD system over the sampling period. It is clear that there is generally less protein in the crude sludge, more in the test reactor, and the largest amount in the TFAS. There is some breakdown of proteins occurring in the ATAD system, as the amount in the test reactor is almost always lower than the combined inputs. The larger amount of protein in the TFAS is due to bacteria absorbing the nitrogen and protein in the wastewater. The nitrogen and amino acids are absorbed and rearranged to make new proteins. The higher amount of protein is likely because of the extra protein content in the biomass and the ability of the bacteria to fix nitrogen from the air and create new amino acids and proteins.

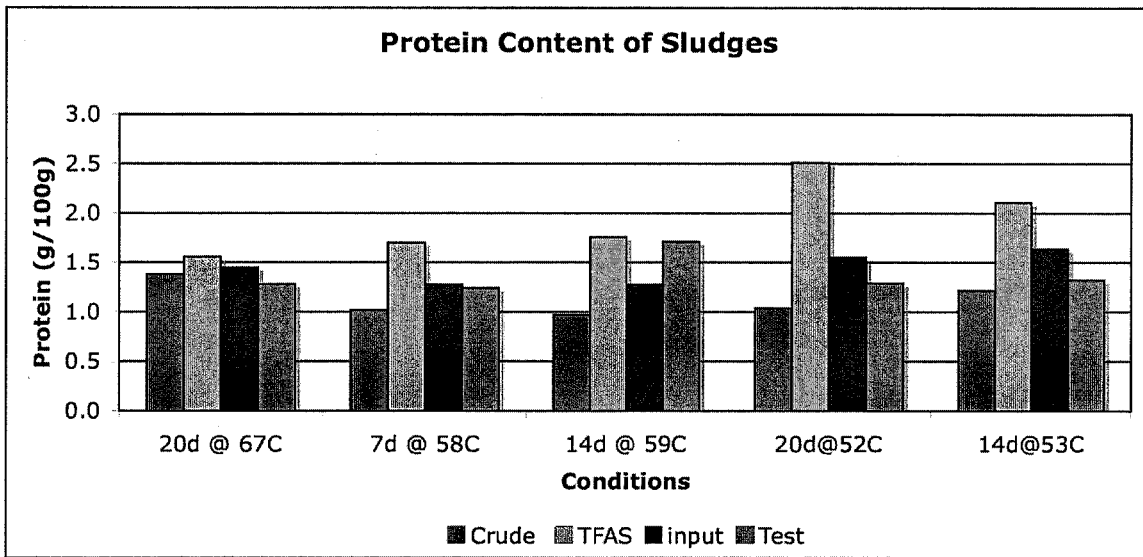


Figure 16: Protein Content of Sludges

There is no significant difference between the protein content in the crude sludge or the TFAS for each condition (F-crit=2.9 & F=1.4 for crude and F-crit=2.9 & F=1.5 for TFAS). However, these samples were taken on the same days as the samples from the test reactor and may not be fully representative of what was fed to the ATAD system during the previous retention time.

4.2.2 Carbohydrates

Figure 17 shows the carbohydrate content of the sludge in the test reactor for each condition. Although there is a lot of variability in the data, the amount of carbohydrates present in the test reactor for each condition is not significantly different (F-crit=2.9 and F=2.2). The carbohydrate content of the crude and TFAS are also not significantly

different between conditions (F-crit=2.9 & F=2.8 for the crude and F-crit=2.9 & F=1.4 for the TFAS).

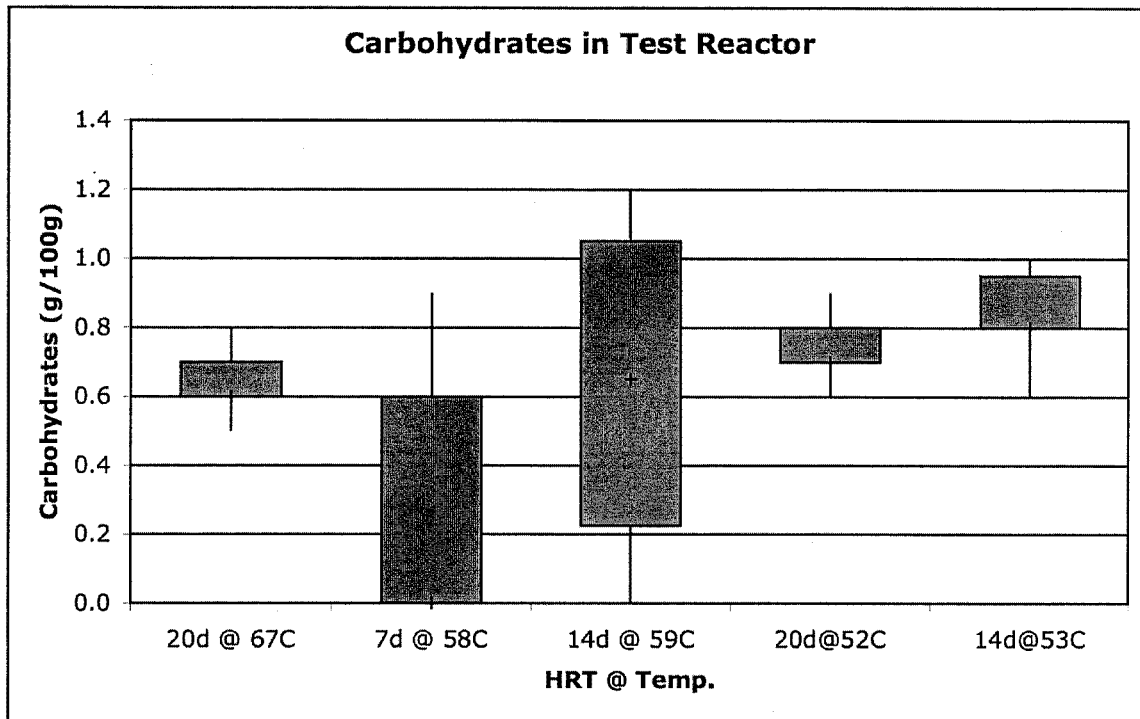


Figure 17: Carbohydrate Content in Test Reactor

Figure 18 shows the carbohydrate content of the various types of sludge for each condition. It is clear that the greatest amount of carbohydrate is present in the crude sludge and that there is significant breakdown of carbohydrates occurring in the ATAD system.

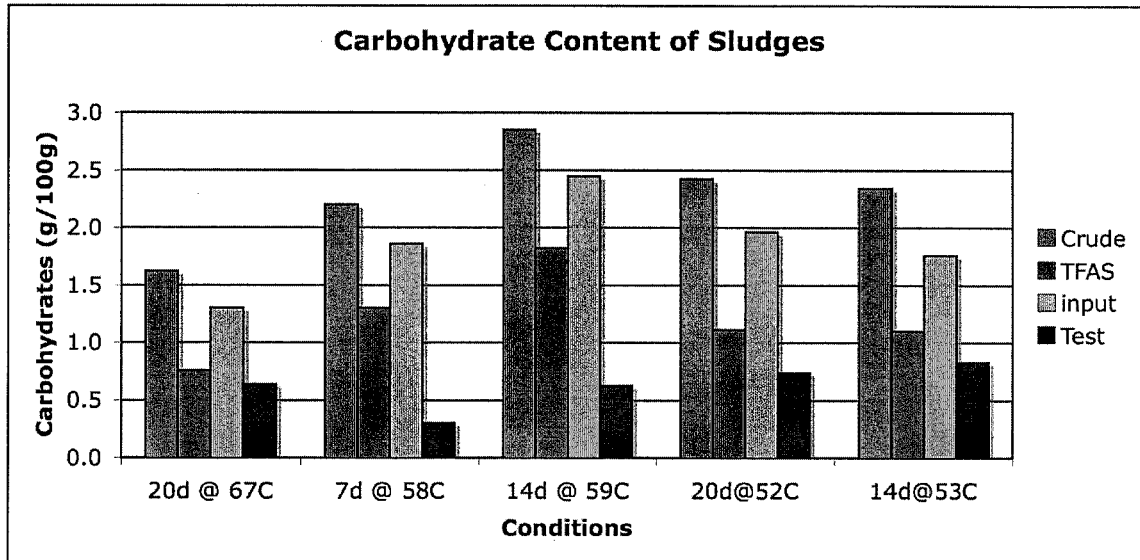


Figure 18: Carbohydrate Content of the various sludges for each condition

4.2.3 Fats

Figure 19 shows the fat content in the test reactor for each condition. There is some variability in the data, but the results indicate that there are no significant differences between conditions (F-crit=2.9 and F=2.2). Although the fat content in the TFAS is not significantly different between conditions (F-crit=2.9 and F=1.7), the fat content of the crude is significantly different between conditions (F-crit=2.9 and F=4.2) (see Figure 20).

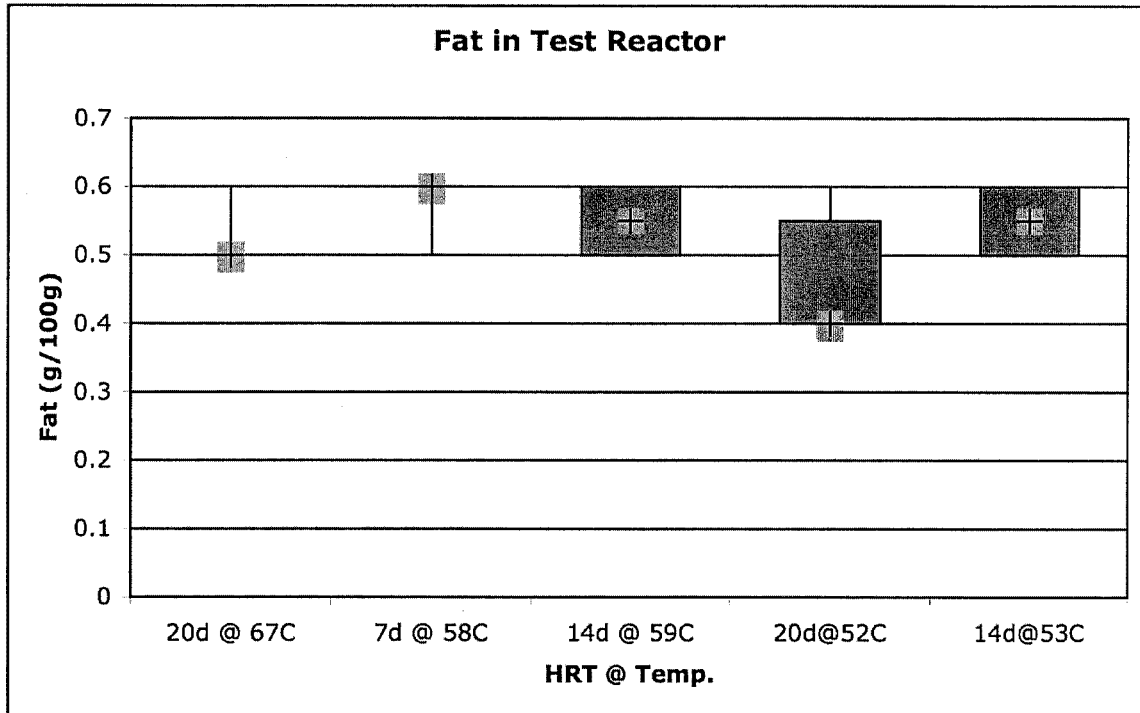


Figure 19: Fat Content in Test Reactor for Each Condition

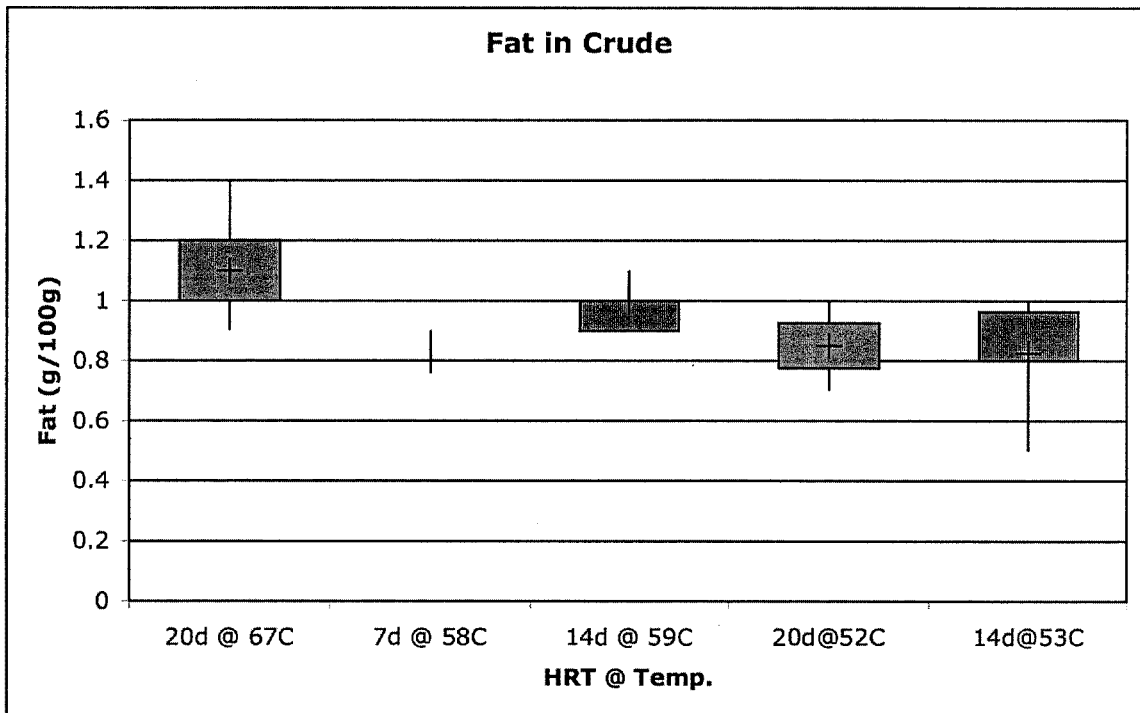


Figure 20: Fat content in Crude Sludge for each Condition

From Figure 20 it appears that the fat content in the crude sludge is higher for the first condition tested, which was confirmed by performing an ANOVA on the last four groups of data only ($F\text{-crit}=3.2$ and $F=1.8$).

Figure 21 shows the fat content of the various types of sludge for each condition. It is clear that the fat content is highest in crude sludge and least in the test reactor. This shows that there is breakdown of fats in the ATAD system.

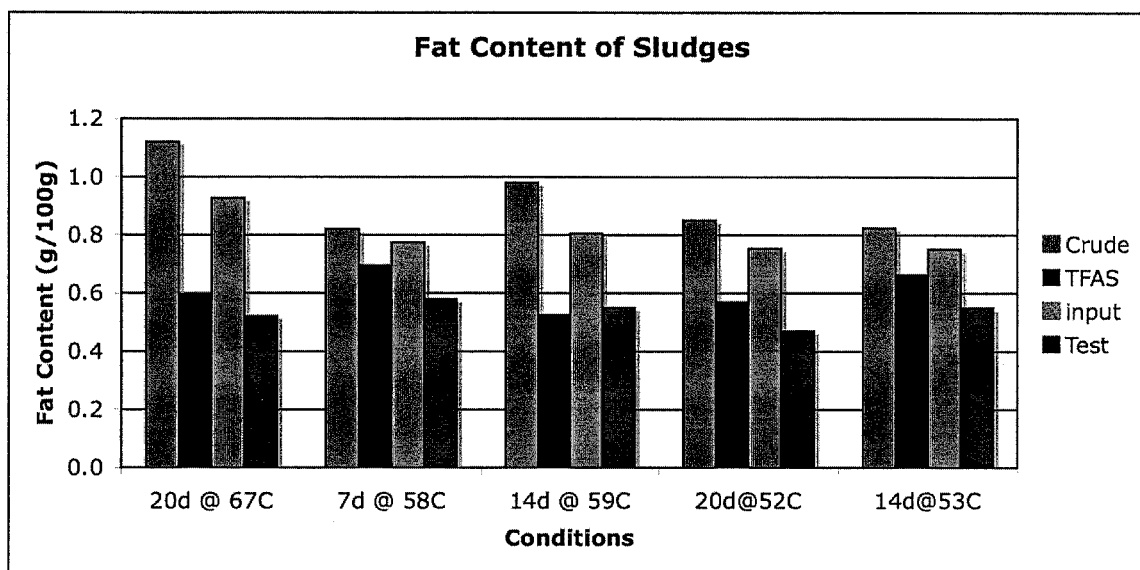


Figure 21: Fat Content of Various Sludges for Each Condition

4.2.4 Discussion

Breakdown of all the macronutrients was observed with the largest breakdown occurring in carbohydrates, followed by fats, and finally proteins. This is because carbohydrates are the simplest of the molecules and provide the most energy, therefore the bacteria present in the reactor chooses to metabolise these molecules first. Proteins are the most complex molecules of the macronutrients, and they are more difficult to break down. However, it is evident that some breakdown is occurring even in the feed reactor, as reduced sulphur compounds (H_2S , CH_3SH , and $(CH_3)_2S$ were measured in this study) are released likely as a result of the breakdown of amino acids.

Carbohydrates, fats and proteins are all broken down through the ATAD process to different degrees. Carbohydrates seem to be the most easily degraded, followed by fats and then protein. It is thought that carbohydrates settle out first, as they are the most prevalent in the crude sludge. Fats settle out as well in the crude sludge, but they are also

found in the TFAS. Very little protein is found in the crude sludge, the largest concentration is found in the TFAS. Most of the protein in wastewater is used by the biomass in the trickling filter. The biomass grows and sloughs off and the protein is then found in the TFAS.

The ATAD process is thought to degrade carbohydrates most, as these are more simple structures made up of carbon and the substrate most needed by the biomass in the system. Fats are degraded less as they are more complex, followed by protein, which are even more complex in their make-up.

4.3 Gases

It was discovered about 3/4 of the way through the study that the sampling method being utilized for gas analysis was incorrect. Because of this, an additional correction factor had to be applied to the data, on top of the temperature corrections. Fortunately, this error was discovered before the end of the study, which allowed correction factors to be developed. The correction factors were developed by using both the “wrong” and the “right” techniques on each of the testing days for the last condition that was run. Dividing the average “right” concentration by the average “wrong” concentration for that condition gave an appropriate correction factor.

On top of the five odorous gases that were monitored volatile fatty acid (VFA) concentration was also measured once during the study period as part of another study that was being started. Samples were taken from each of the reactors in the process except for the test reactor. It was found that the VFA concentration was over twice as high in the feed reactor than in any of the other reactors. The normal process train is from reactor 4 to 5 to 3 to 1 suggesting that the acid content is drastically reduced through the process but increases again at the end.

Table 3: VFA results

Reactor	Total VFA as acetic (mg/L)
ATAD 1	867
ATAD 3	112
ATAD 4	2332
ATAD 5	742

4.3.1 Hydrogen Sulphide

Figure 22 shows the approximate hydrogen sulphide (H_2S) concentrations in the test reactor, for each of the five conditions tested. These results were developed using the correction factors discussed above. The results of an ANOVA show that these results are not significantly different ($F\text{-crit}=2.8$ and $F=1.1$). The data presented suggests that, perhaps, lower temperatures produce higher amounts of H_2S . However, when an ANOVA is done on the results of the first and fourth condition (20d@67C and 20d@52C), these results are not significantly different ($F\text{-crit}>F$).

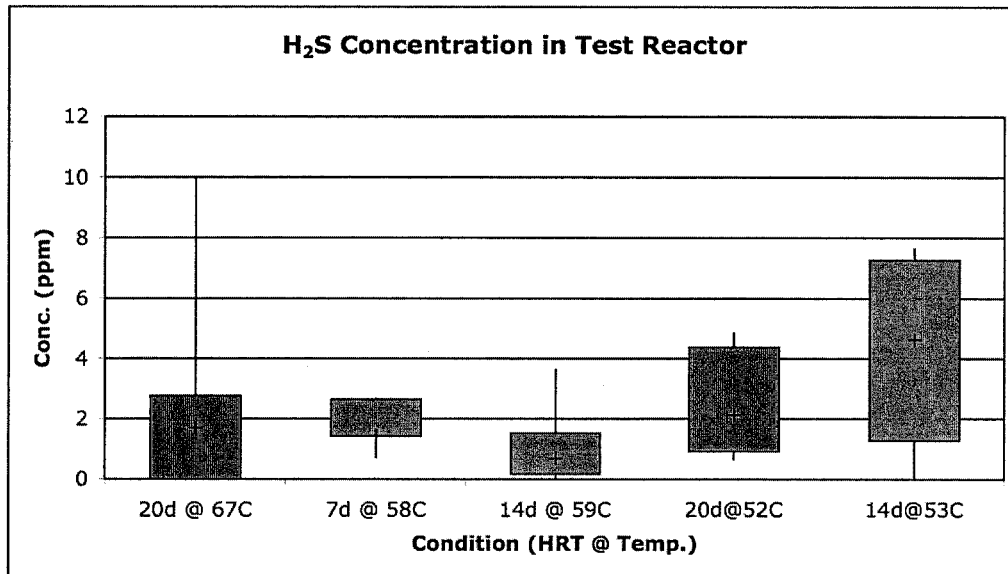


Figure 22: Box and Whisker Diagram of Hydrogen Sulphide Concentrations in Test Reactor

Figure 23 shows the hydrogen sulphide concentration in the feed reactor. These measurements were taken on the same days as the measurements for the test reactor and therefore, do not account for HRT. These results are also “approximate” and were

corrected using the temperature and method correction factors. As expected, the results are not significantly different for each condition ($F\text{-crit} > F$). However, there is a large difference, almost a factor of ten, in the range of concentration values found in the feed reactor and the test reactor. This is attributed to the fact that the sludge in the feed reactor is in an earlier state of digestion (see discussion in Section 4.3.6).

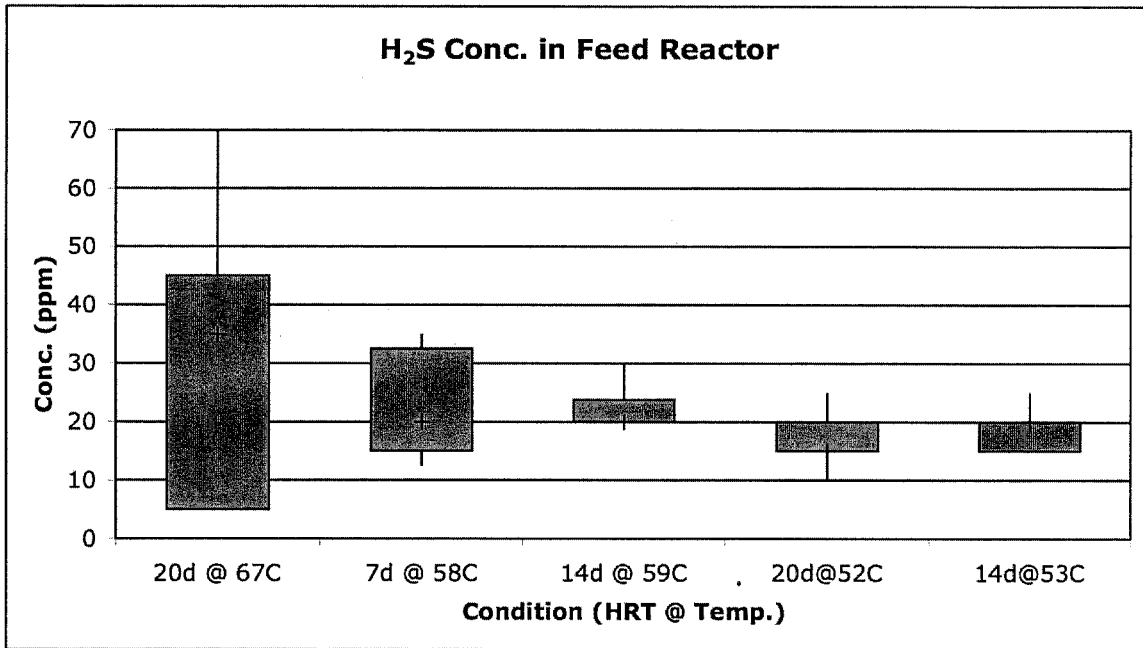


Figure 23: H₂S Concentration in the Feed Reactor

Figure 24 shows the two sets of results obtained for the last condition tested. The first set of results was obtained using the “wrong” method and then the correction factors were applied. The second set was obtained correctly and only temperature corrections were applied. This figure shows that the range of the results is concentrated, and the median is adjusted, but that the majority of results are in the same range when the correction factor is applied. This indicates that although the method used was improper the results found are still valuable and could be used for comparison, but not as absolute values.

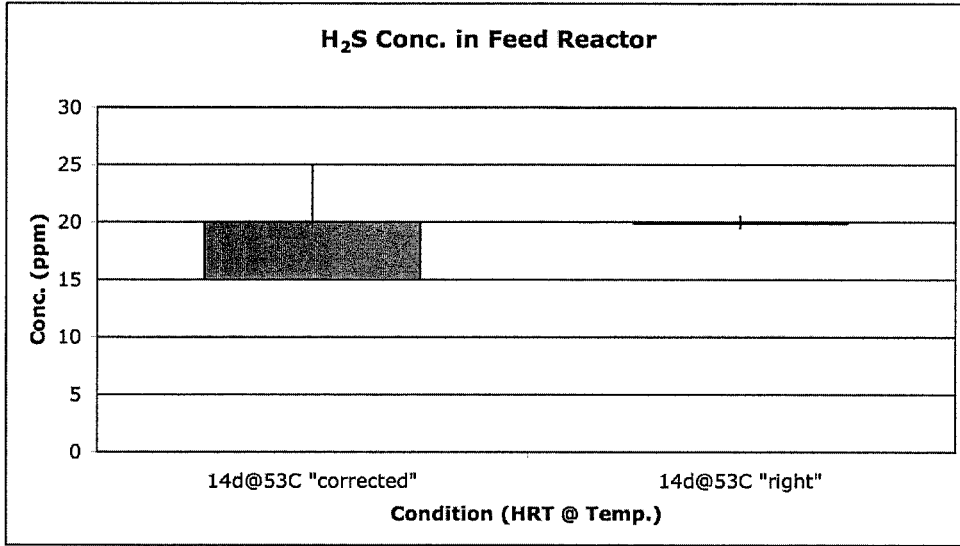


Figure 24: Corrected and Right Concentrations of H₂S in Feed Reactor

4.3.2 Methyl Mercaptan

Methyl mercaptan (CH_3SH) is one of the most odorous gases produced by ATAD systems and is also one of the gases that cause “bad breath”. Figure 25 shows the variations in methyl mercaptan concentrations found for each condition tested. These data have been corrected for improper measurement technique and temperature. An ANOVA done on the data shows that methyl mercaptan concentration is not significantly affected by changes in temperature or retention time ($F\text{-crit}=2.9$ and $F=2.6$). It does seem, from comparing the results, that shorter retention times produced lower amounts of CH_3SH , but when comparing groups at the same temperature but different HRTs, the results for 7d@58C are not consistent with this. Also, an ANOVA done on 20d@52C and 14d@53 shows that these are not significantly different ($F\text{-crit} > F$).

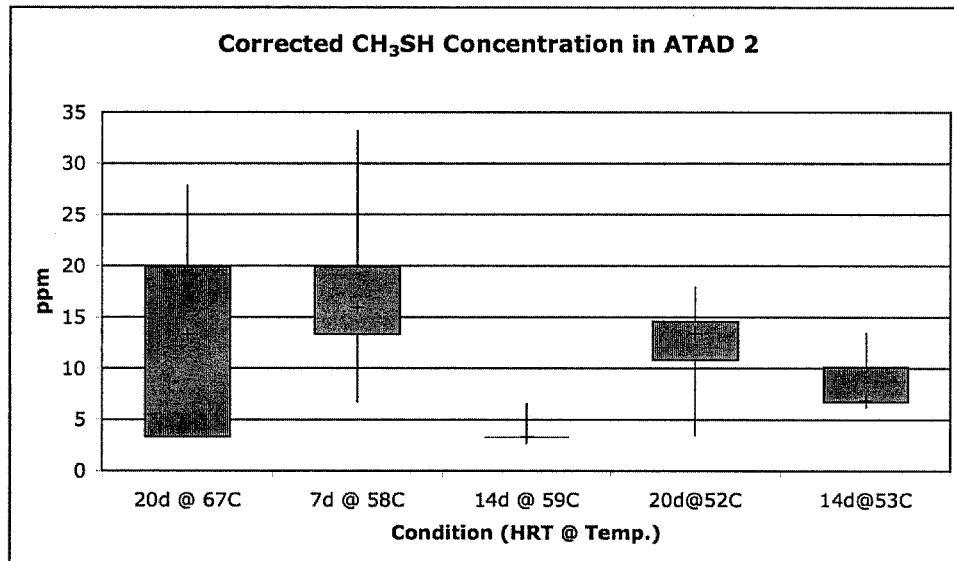


Figure 25: Methyl Mercaptan Concentrations in Test Reactor

Figure 26 shows the methyl mercaptan concentrations in the headspace of the feed reactor on the same days as the concentration was measured in the test reactor. An ANOVA done on these results show that they are not significantly different ($F\text{-crit} > F$). Performing an ANOVA on 14d@59C and 14d@53C shows these are significantly different but this is not true of 20d@67C and 20d@52C. Therefore, changes in HRT or temperature do not result in significant differences in methyl mercaptan concentrations.

However, the concentrations in the headspace of the test reactor are lower than those found in the headspace of the feed reactor, a difference of about three times.

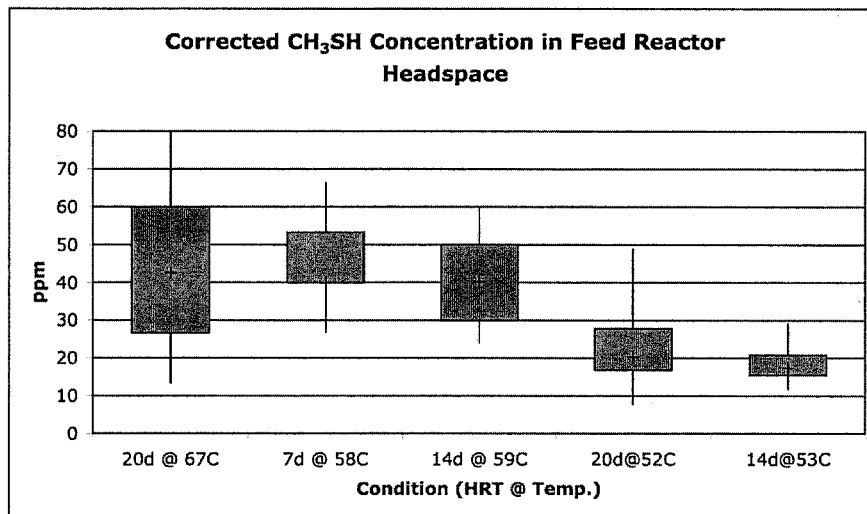


Figure 26: Methyl mercaptan concentrations in the Feed Reactor Head Space

Figure 27 shows a comparison of the corrected data and the more accurate data for methyl mercaptan concentration in the test reactor for the last condition tested. This figure shows that the median is almost the same, however the corrected results seem to be skewed upwards (to the right).

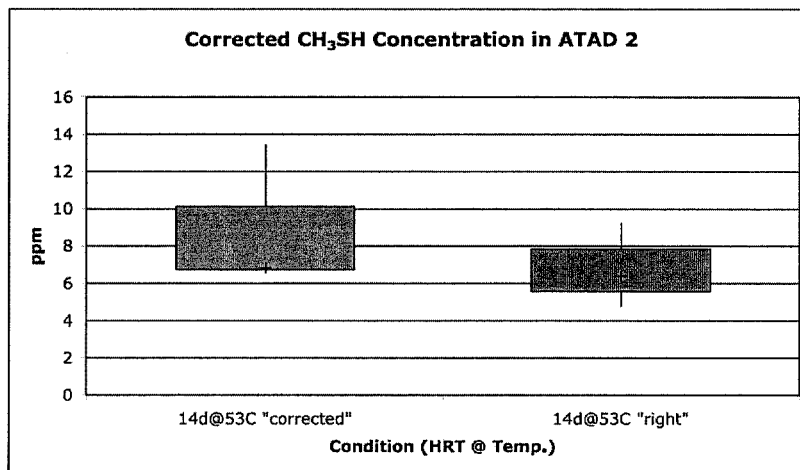


Figure 27: Comparison of Corrected and "Right" Concentrations of CH₃SH in Test Reactor

4.3.3 Ammonia

Figure 28 shows the variation in ammonia gas concentrations measured in the test reactor for each condition. An ANOVA done on the results shows that they are significantly different ($F\text{-crit}=2.8$ and $F=3.6$). From the figure, this difference seems primarily due to temperature. An ANOVA done on the first and fourth condition and another done on the third and fifth condition, confirms this ($F\text{-crit} < F$ for both). This is a natural relationship wherein the heat energy available at higher temperatures is used by ammonia to allow it to transition into the gas phase. Although the boiling point of ammonia is very low ($-33\text{ }^{\circ}\text{C}$), its heat of vaporization is quite high, indicating that it requires the extra heat to volatilize.

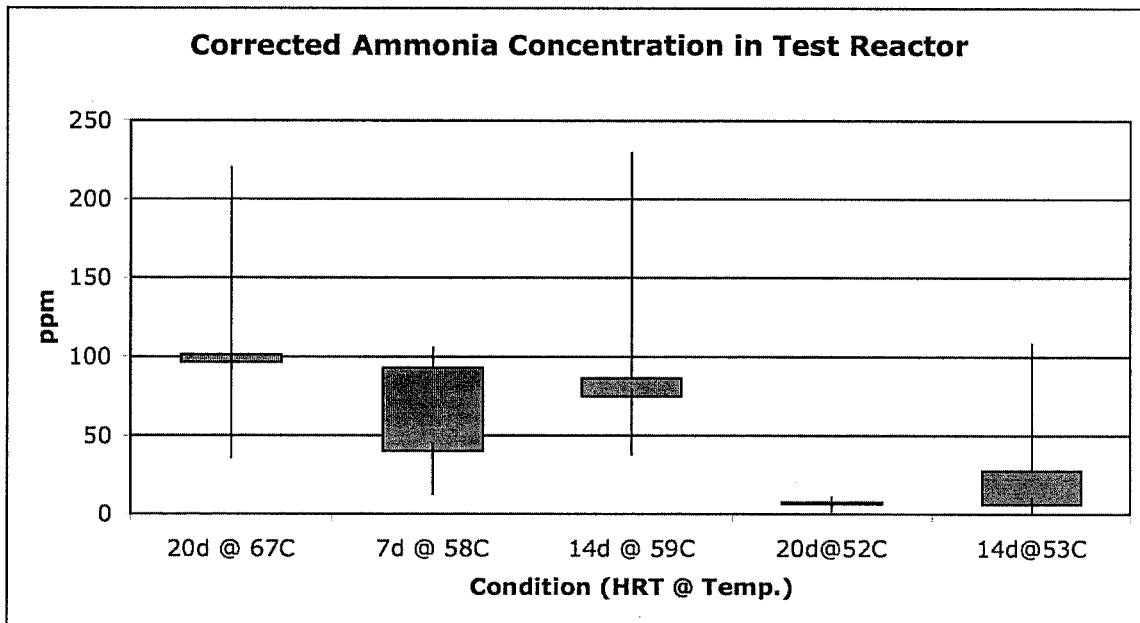


Figure 28: Ammonia Concentrations in Test Reactor

Figure 29 shows the variation in ammonia concentration in the feed reactor for each condition. These results follow the same pattern as those observed in the test reactor, although the concentrations are very different. One reason for this could be that for the last two conditions tested the temperature in the feed reactor was significantly lower (33 and 37°C versus 45 and 46°C). At lower temperatures there is less heat energy available to drive the conversion of liquid ammonia to gaseous ammonia. With a higher

concentration of ammonia in the gas phase, more is being removed through the exhaust system to be treated and this drives the reaction to create more gaseous ammonia. At lower temperatures, the heat energy is not available to maintain this reaction.

The concentrations in the feed reactor are significantly different ($F\text{-crit}=2.8$ and $F=3.5$); however, when only the first three groups are compared, they are not ($F\text{-crit} > F$). It seems that the feed, for the last two conditions, released almost no ammonia, and in general the concentrations are much lower than in the test reactor. It is understood from these results that ammonia gas is mostly formed through the deamination of proteins occurring in an ATAD reactor, which occurs more in the higher temperature test reactor than the feed reactor.

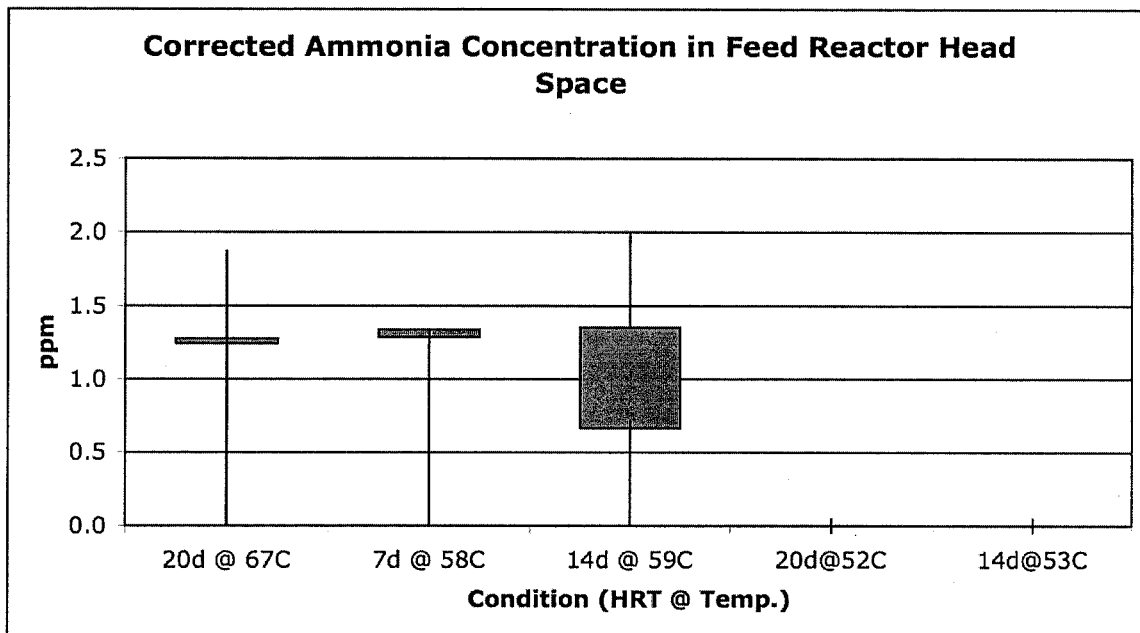


Figure 29: Ammonia Concentration in Head Space of Feed Reactor

The high concentrations of ammonia in the test reactor could be caused by a variety of things, including the concentration in the feed reactor, the ammonia concentration in the liquid, the reactor pH, and protein content. Looking back at Figure 11 (copied again as Figure 30) the ammonia concentration in the liquid actually appears to be higher for the lower temperatures. This may not seem intuitive but can be explained by the ammonia / ammonium balance. Since ammonia exists more commonly in the gaseous phase, when the extra energy is available at higher temperatures, the

ammonia present in solution goes into the gaseous phase, leaving a lower concentration in the liquid. So, the higher concentrations could be caused, in part, by the temperature difference, and thereby affect the liquid concentration.

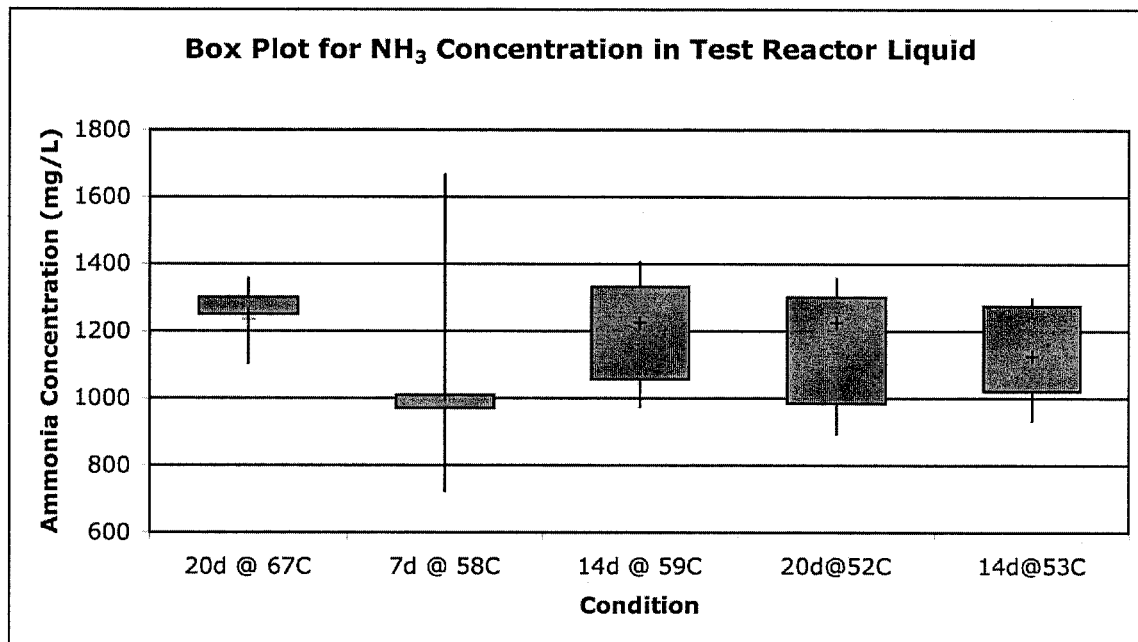


Figure 30: Ammonia Concentration in the test reactor Liquid

The high ammonia gas concentration could also be caused by changes in pH; when pH is higher, more ammonia gas is formed. However, for the high temperature conditions, the pH is not significantly different from the other conditions, except for the first condition (see Figure 31).

The high concentration could potentially be due to the amount of protein in the feed; however the protein content of the crude and TFAS was not significantly different between conditions and so there doesn't seem to be a relationship. Therefore, it appears that the high ammonia concentrations are caused by a high pH in some circumstances and high temperature in others, indicating a dependence on "reactor state". The reactor state or health can be described by: the balance of oxidative and fermentative reactions occurring, the amount of mixing and air supply, a good SOUR, and the ratio of H₂S to NH₃ gas in the headspace.

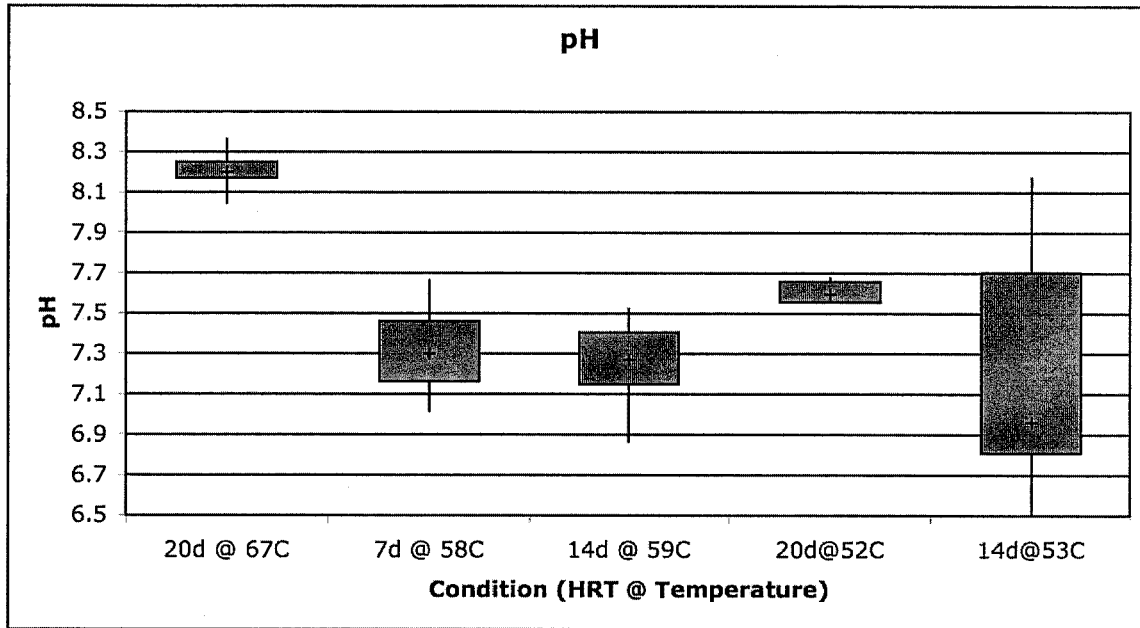


Figure 31: pH of the Test Reactor Liquid

Figure 32 shows the corrected and “right” concentration of ammonia gas in the headspace of the test reactor for the last condition. The correction brings the results close to the correct values, but not completely. It is also clear that there is no way to account for the randomness of the results or outliers, with this type of correction factor.

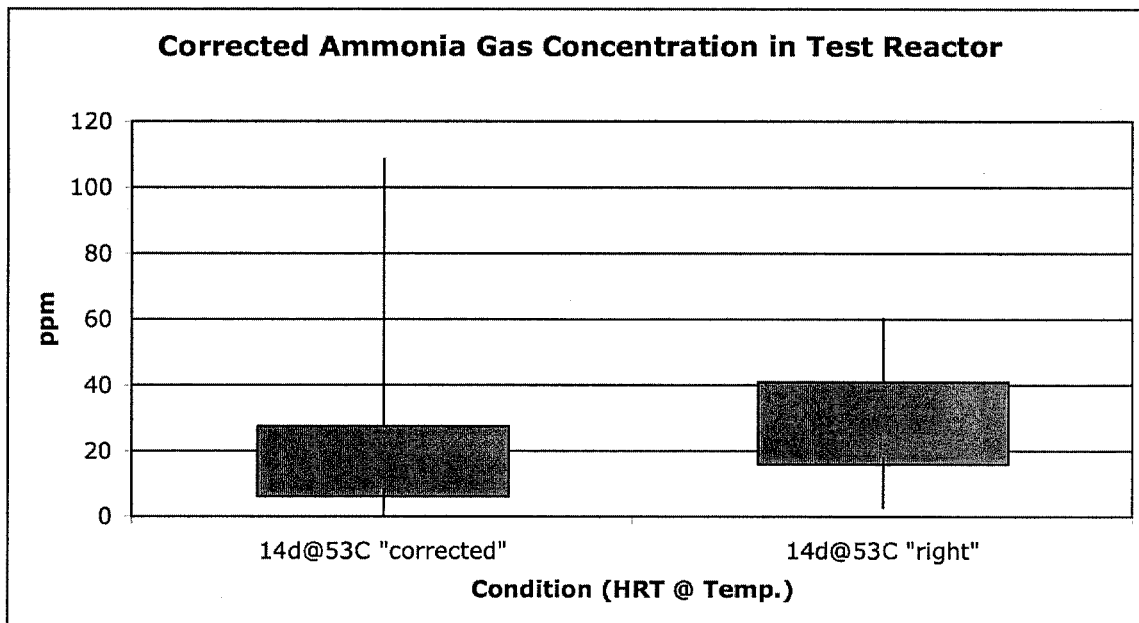


Figure 32: Corrected and "Right" Concentration of Ammonia in Test Reactor

4.3.4 Amines

Figure 33 shows the various “corrected” amine concentrations in the test reactor for each condition. These overall results are significantly different (F-crit=2.8 and F=15.5); however the first three groups are not (F-crit=3.8 and F=0.3).

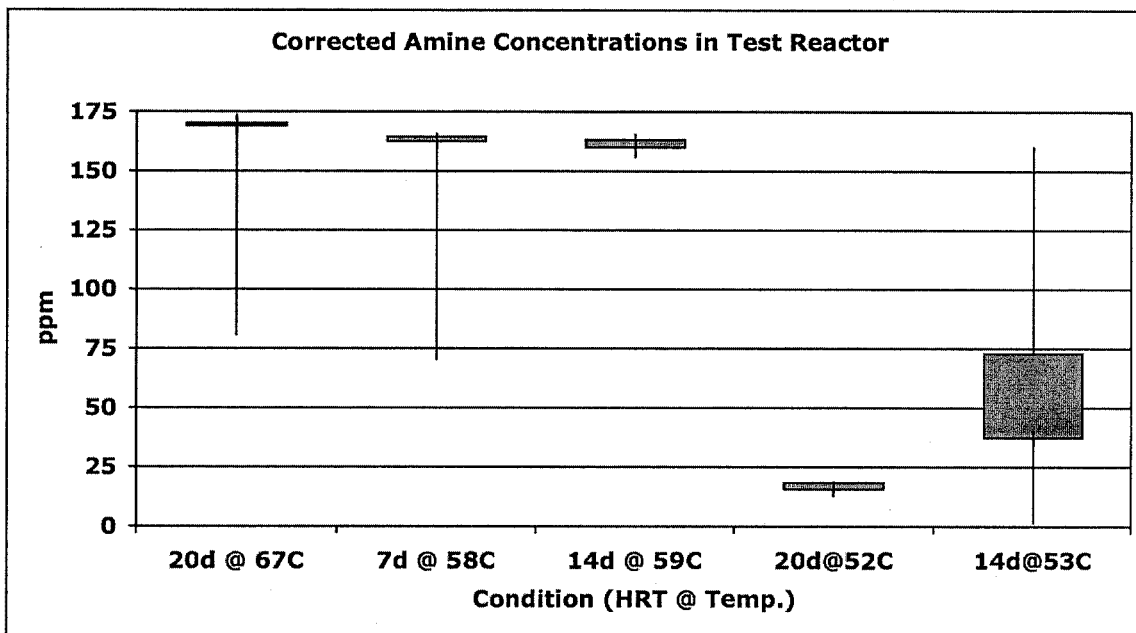


Figure 33: Amine Concentration in Test Reactor

Figure 34 shows the corrected amine concentrations in the feed reactor for each condition. It is clear that the amine concentrations in the feed reactor are much lower than those found in the test reactor. These results are not significantly different (F-crit=2.8 and F=0.9), indicating that changes in temperature or HRT do not seem to affect amine concentration in the feed reactor.

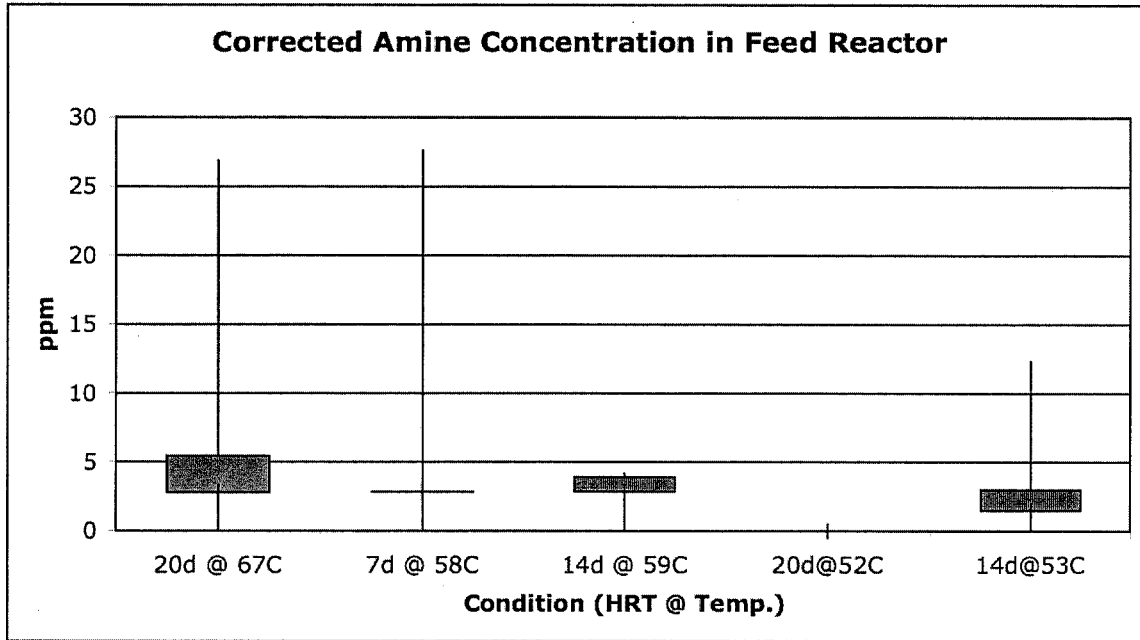


Figure 34: Amine Concentrations in Feed Reactor

Figure 35 compares the corrected with the actual concentration of amines in the feed reactor for the last run. The “corrected” results have had the measurement correction and a temperature correction applied, while the “right” results have only the temperature correction. It is clear that the measurement correction is not perfect, but does keep the median close and gives a similar range of results.

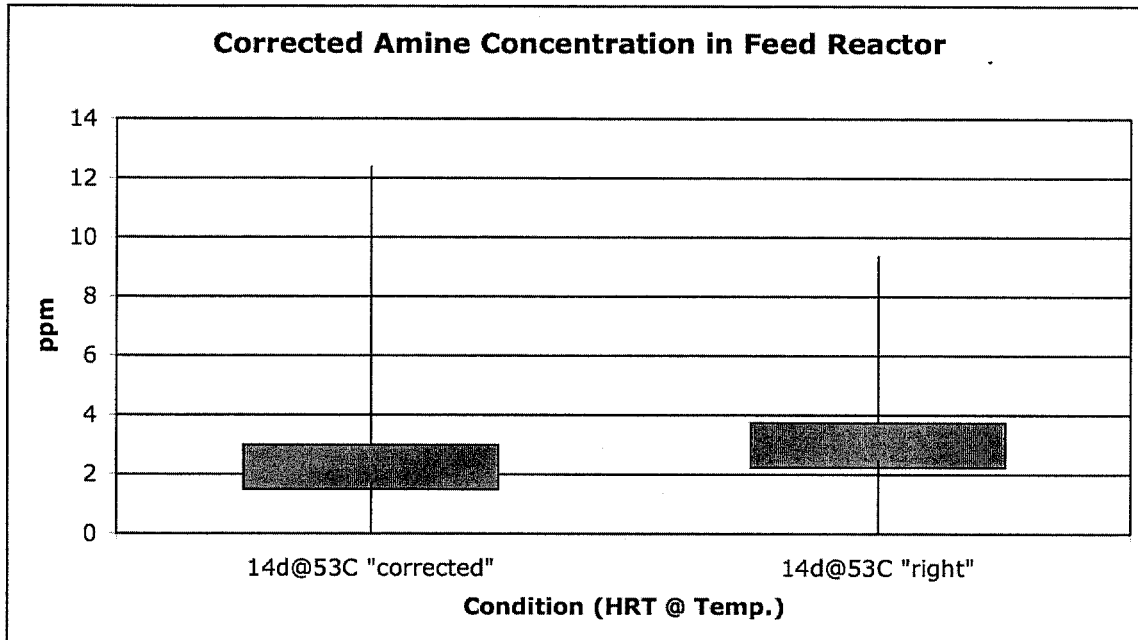


Figure 35: Corrected and "Right" Concentrations of Amines in Feed Reactor

4.3.5 Dimethyl Sulphide

Figure 36 shows the corrected dimethyl sulphide concentrations in the test reactor for each condition. The total results are significantly different ($F\text{-crit}=2.9$ and $F=3.4$); however, the last four groups are not ($F\text{-crit}=3.2$ and $F=1.7$). The corrections for this data were done differently than for the other gases because the concentrations were so low. Instead of dividing the average of the "right" results by the "wrong" ones, the difference between the means was added to the "wrong" ones, since many of those results were zeros.

Because the measurements of dimethyl sulphide required an extra piece of equipment that did not arrive until after the beginning of the study, there are only three data points that contribute to the first group of data; therefore, it would not be wise to base any conclusions on so few data points.

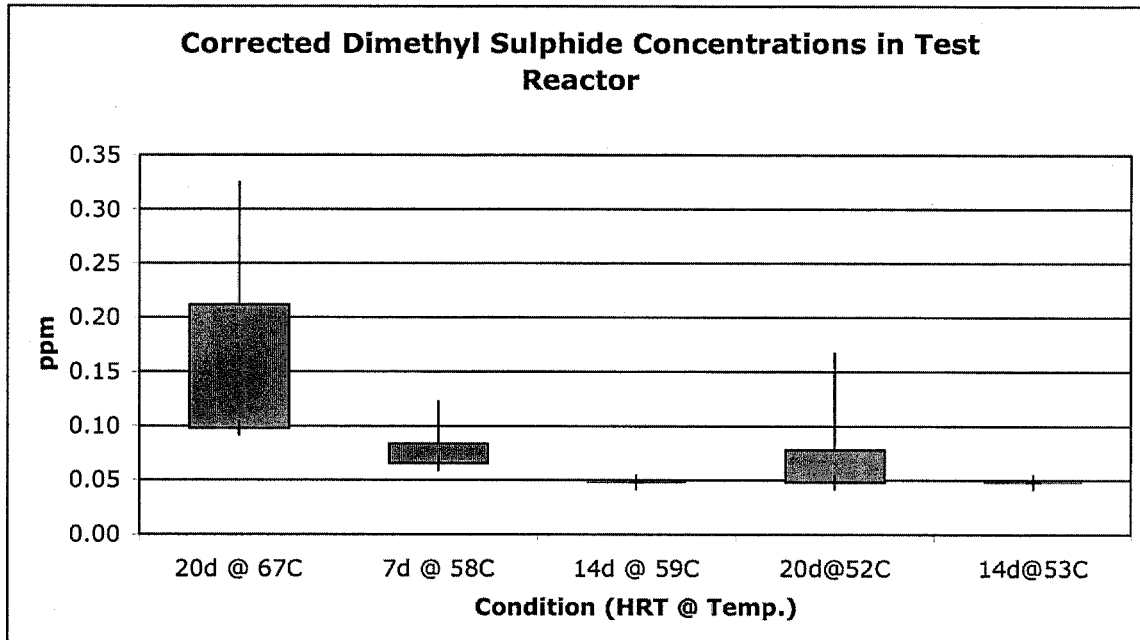


Figure 36: Corrected Dimethyl Sulphide Concentrations in Test Reactor

Figure 37 shows the dimethyl sulphide concentrations found in the feed reactor for each condition. The measurement corrections applied to these results are the same as those done for the test reactor (the difference between the means was used instead of the quotient). These results are significantly different ($F\text{-crit}=2.9$ and $F=10.4$). The difference could be caused directly by temperature, as the first three groups are not significantly different ($F\text{-crit}=4.0$ and $F=0.5$) and neither are the last two groups; they are identical. The concentrations measured in the test reactor are also lower than those in the feed reactor.

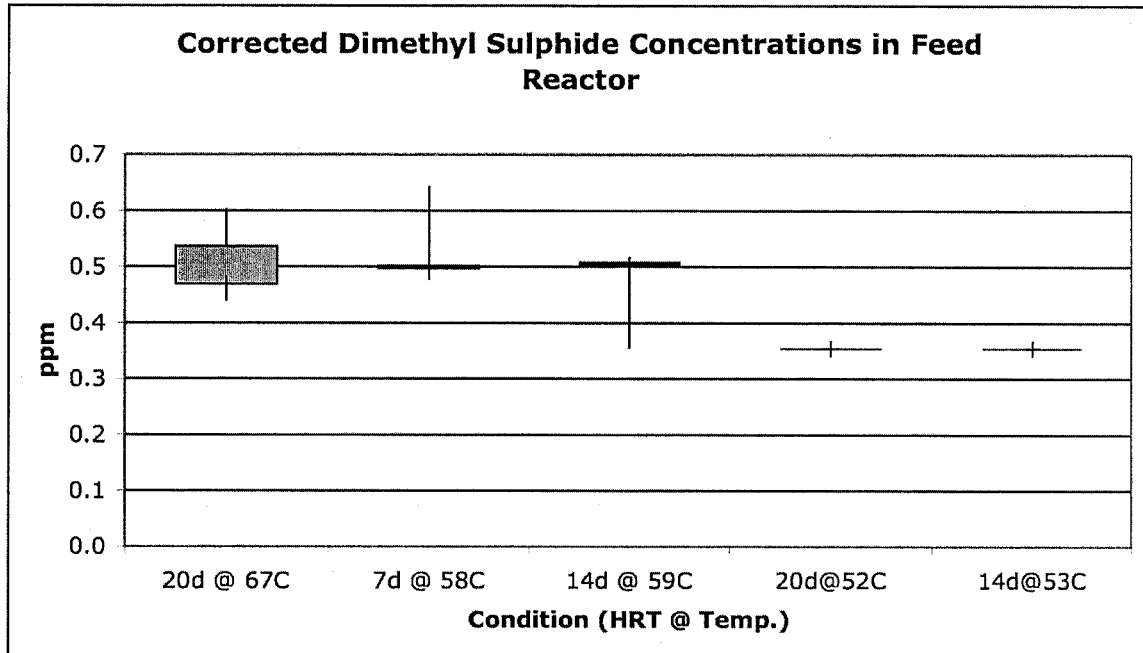


Figure 37: Dimethyl Sulphide Concentrations in Feed Reactor

Figure 38 shows the corrected and “right” results for dimethyl sulphide concentration in the feed reactor for the last condition tested. It is clear that the correction factor applied can adjust the mean, but there is no way of correcting for the variance in the results. For this data, all the results were zero, using the “wrong” method, so all that can be done is to adjust them upward.

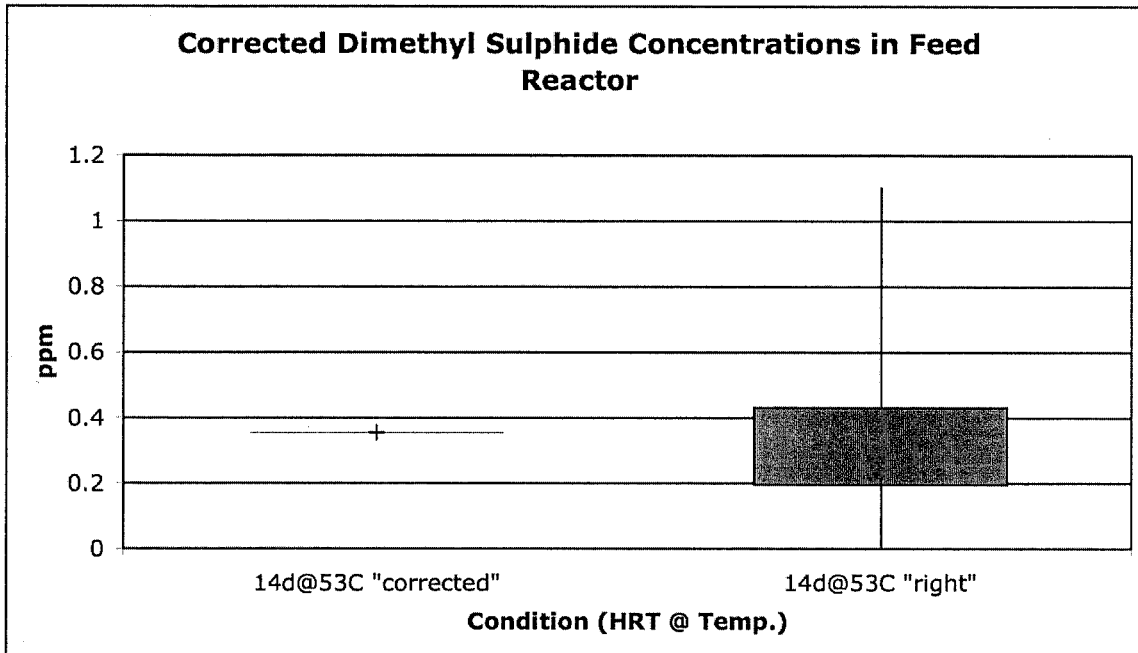


Figure 38: Comparison of Dimethyl Sulphide Concentrations

4.3.6 Discussion

Hydrogen sulphide, methyl mercaptan, and dimethyl sulphide concentrations were found to be higher in the feed reactor than in the test reactor. Simultaneously, amine and ammonia concentrations were much higher in the test reactor than the feed reactor. This is attributed to the different stages of protein breakdown, as mentioned in Section 4.2.

Carbohydrates and fats are more easily broken down than proteins and that is why there is a greater amount of breakdown seen through the process. However, the initial breakdown of proteins into amino acids results in the release of reduced sulphur compounds. Later in the process, at higher temperatures, proteins are further metabolized, or deaminated resulting in the release of amines and ammonia gas.

Staton et al. (2001) suggest that a healthy reactor gives off higher concentrations of ammonia gas and lower concentrations of reduced sulphur compounds. In this study, ammonia gas concentrations were higher at higher temperatures in the feed reactor and the test reactor. If Staton is correct, since greater amounts of ammonia are produced at higher temperatures then higher temperatures must lead to a healthier reactor. This seems to be in accordance with the SOUR results. Because this trend of higher ammonia gas

concentrations at higher temperatures is also observed in the feed reactor, it is clear that heat energy is required for ammonia to move into the gaseous phase.

Although an incorrect method was initially used for collecting most of the results, once the method correction factor was applied, the results are considered acceptable.

5 Conclusions and Recommendations

5.1 Conclusions

Based on the results from the various conditions run, we can draw several conclusions.

- Of the various measures of stability that were used (Specific Oxygen Uptake Rate (SOUR), Volatile Solids Content, and Volatile Solids reduction), a plot of volatile solids reduction versus the number of Hydraulic Retention times (HRT) elapsed gives the clearest indication of when stability is achieved. However, the best way to assess stability in the reactor is a combination of SOUR, VS, and VS reduction.
- SOUR results seem to be lower for higher temperatures (above 55°C) suggesting the sludge is more stable at these higher temperatures.
- Volatile solids destruction was observed to be lower at higher temperatures, the reasons for this are not completely understood but it is thought that the variation in volatile solids in the feed plays a key role.
- Total solids destruction was observed to be dependent on HRT and not temperature.
- Ammonia concentration in the liquid is not affected by changes in HRT or Temperature.
- Alkalinity and pH are affected by the dissociation of H₂S and CO₂ respectively.
- The carbohydrate, protein, and fat concentration of the test reactor sludge was not significantly affected by changes in HRT or Temperature. In general, the greatest amount of carbohydrates and fats were present in the crude sludge, and the greatest amount of proteins was found in the trickling filter activated sludge (TFAS). In general, carbohydrates seem to be the easiest to breakdown, followed by fats, and then proteins.
- From the gases analysed, it seems that reduced sulphur compounds are released earlier in the process, potentially during the breakdown of proteins into amino acids. In the second reactor there are very high concentrations of ammonia and amines, likely as a result of the deamination of proteins.

- The concentration of hydrogen sulphide, methyl mercaptan, and dimethyl sulphide produced seems to be dependent on the temperatures of the reactor in which it is measured. They are not influenced by changes in temperature between 35 and 45°C however, smaller concentrations were measured in the test reactor which was operated at higher temperatures (between 50 and 70°C). The concentrations produced do not seem to be affected by changes in HRT in the test reactor, likely because their production is limited at these high temperatures. Essentially the same concentrations were produced whether the HRT in the test reactor was 3d or 17d. This shows that each completely mixed reactor acts as a stage in the process with various operating conditions and off gases produced. Together the reactors approach a plug flow system and the off gases produced can be an indication of the stage of treatment.
- The amount of ammonia and amines produced is significantly higher at higher temperatures than at lower temperatures. This is likely caused by the conversion of liquid ammonia to gaseous ammonia, which is pulled off in the exhaust system, driving the reaction to produce more gaseous ammonia.
- The concentration of ammonia gas and dimethyl sulphide gas produced in the feed reactor is lower at lower temperatures. For both of these compounds, the concentrations measured in the feed reactor were lower for the last two conditions; both included average temperatures below 40°C in the feed reactor.

5.2 Recommendations

Recommendations made as a result of this research fall in operational and research categories.

Operationally, it was found that the sludge was observed to be more stable when the reactor, where most of the digestion occurs (in this case the test reactor), is operated at higher temperatures (above 55°C). However, at these high temperatures, greater amounts of ammonia and amines are given off as gases, as a result of the high temperatures and pH. Because stability of the sludge is essential and these odours are not difficult to treat, operation at these temperatures may be acceptable.

Also, in this study it was only possible to test one reactor configuration, it would be useful to know if different reactor configurations produce different types or quantities of odorous gases. Further studies are also required to determine if one reactor would produce reduced odours than two or more in series.

Another operational question that should be addressed is: are there benefits to operating the reactors under pressure? This could reduce the gas released and allow the use of pure oxygen, which may result in more complete oxidation of some of the odorous compounds. This would require operating a pressurized reactor and non-pressurized reactor, under similar conditions, and monitoring both the odours and the by-products of digestion.

One of the original objectives of this study was to investigate the operation of an ATAD system at very high temperatures. In this study, the highest average temperature that was achieved was 71°C in the test reactor. However, if a similar study was conducted at a bench scale, potentially higher temperatures could be reached. ATAD operators and designers may be interested in knowing the characteristics of odours that are produced at temperatures above 70°C, since, it is understood that, above this temperature a greater breakdown in protein is possible.

One of the main tests used for measuring stability of the process and of the sludge was Specific Oxygen Uptake Rate (SOUR). Although this test was very useful, it was very difficult to carry out, for some conditions. There is also a question as to the validity of the results, since the test was typically performed at lower temperatures than the test reactor was operated; this would have an effect on the bacterial community. For these reasons, an interesting and extremely useful project would be to develop a different test for measuring the oxygen uptake rate of the sludge at these higher temperatures. The goal of this test is to assess the demand the biosolids will place on the soil to which they are added. If there is a high oxygen demand, the biosolids will also use nutrients from the soil. One option, therefore, might be to monitor the nitrogen or phosphorus concentration and uptake in the soil, as an indirect method of assessing the oxygen demand.

Another indicator of stability is volatile solids reduction; however, the amount of reduction observed in this study was consistently less than expected for the time and

temperature conditions used. Therefore, it is recommended that a targeted amount of reduction should not be used as a measure of stability. Instead, achieving the same amount of reduction consistently could be used as an indicator of stability.

Additionally, this study examined the production of odorous gases as a result of the breakdown of proteins. More research is needed into what gases are produced from the breakdown of carbohydrates and fats, perhaps carbonyl sulphide and carbon dioxide. As well, more research is needed to have a better understanding of the exact mechanisms involved in protein breakdown. This would likely have to be done under very controlled circumstances to assess the impacts of parameters such as time and temperature.

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Appendix A: Specific Oxygen Uptake Rate (SOUR)

Specific Oxygen Uptake Rate (SOUR) based on VS

SOUR (VS)	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.181	0.099	0.378	1.551	1.003
	0.178	0.118	0.309	1.108	0.382
	0.205	0.221	0.163	1.407	0.443
	0.468	0.361	0.319	1.659	0.976
	0.547	0.434	0.444	0.770	0.648
			0.393	0.973	
Median	0.2	0.2	0.3	1.3	0.6
q1	0.2	0.1	0.3	1.0	0.4
min	0.2	0.1	0.2	0.8	0.4
max	0.5	0.4	0.4	1.7	1.0
q3	0.5	0.4	0.4	1.5	1.0

ANOVA on All Groups

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	1.579	0.316	0.031
7d @ 58C	5	1.234	0.247	0.022
14d @ 59C	6	2.006	0.334	0.010
20d@52C	6	7.467	1.245	0.122
14d@53C	5	3.451	0.690	0.084

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.976	4	0.994	18.098	0.000	2.817
Within Groups	1.208	22	0.055			
Total	5.185	26				

ANOVA on Four Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	1.579	0.316	0.031
7d @ 58C	5	1.234	0.247	0.022
14d @ 59C	6	2.006	0.334	0.010

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>
Between Groups	0.022	2	0.011	0.560	0.584
Within Groups	0.261	13	0.020		
Total	0.283	15			

ANOVA on Three Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	1.579	0.316	0.031
7d @ 58C	5	1.234	0.247	0.022
14d @ 59C	6	2.006	0.334	0.010

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.022	2	0.011	0.560	0.584	3.806
Within Groups	0.261	13	0.020			
Total	0.283	15				

ANOVA on Two Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	6	2.006	0.334	0.010
14d@53C	5	3.451	0.690	0.084

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.345	1	0.345	8.072	0.019	5.117
Within Groups	0.385	9	0.043			
Total	0.730	10				

SOUR based on TS

SOUR (TS)	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.391	0.075	0.278	1.114	0.709
	0.351	0.087	0.227	0.801	0.276
	0.154	0.164	0.122	1.017	0.331
	0.135	0.275	0.234	1.199	0.714
	0.134	0.343	0.329	0.563	0.471
			0.290	0.692	
Median	0.2	0.2	0.3	0.9	0.5
q1	0.1	0.1	0.2	0.7	0.3
min	0.1	0.1	0.1	0.6	0.3
max	0.4	0.3	0.3	1.2	0.7
q3	0.4	0.3	0.3	1.1	0.7

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	1.1639	0.2328	0.0161
7d @ 58C	5	0.9438	0.1888	0.0137
14d @ 59C	6	1.4798	0.2466	0.0052
20d@52C	6	5.3876	0.8979	0.0631
14d@53C	5	2.5006	0.5001	0.0423

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	2.025	4	0.506	17.685	0.000	2.817
Within Groups	0.630	22	0.029			
Total	2.655	26				

ANOVA for Four Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	1.164	0.233	0.016
7d @ 58C	5	0.944	0.189	0.014
14d @ 59C	6	1.480	0.247	0.005
14d@53C	5	2.501	0.500	0.042

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.300	3	0.100	5.401	0.009	3.197
Within Groups	0.314	17	0.018			
Total	0.614	20				

ANOVA on Three Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	1.164	0.233	0.016
7d @ 58C	5	0.944	0.189	0.014
14d @ 59C	6	1.480	0.247	0.005

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.010	2	0.005	0.432	0.658	3.806
Within Groups	0.145	13	0.011			
Total	0.155	15				

ANOVA on Two Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	6	1.480	0.247	0.005
14d@53C	5	2.501	0.500	0.042

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.175	1	0.175	8.093	0.019	5.117
Within Groups	0.195	9	0.022			
Total	0.370	10				

Appendix B: Solids Destruction

Volatile Solids Destruction

VS redn	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	35.411	27.673	29.805	37.563	
	22.702	30.962	27.689	35.634	53.653
	29.168	25.355	32.634	34.609	48.396
	21.898	12.905	30.425	31.732	39.838
	28.172		29.918	36.934	34.880
Median	28	27	30	36	44
q1	23	22	30	35	39
min	22	13	28	32	35
max	35	31	33	38	54
q3	29	28	30	37	50

ANOVA on All Groups

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	137.351	27.470	30.052
7d @ 58C	4	96.895	24.224	62.230
14d @ 59C	5	150.470	30.094	3.114
20d@52C	5	176.472	35.294	5.278
14d@53C	4	176.767	44.192	70.949

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1011.296	4	252.824	8.225	0.001	2.928
Within Groups	553.318	18	30.740			
Total	1564.615	22				

ANOVA on Four Groups
SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	137.351	27.470	30.052
7d @ 58C	4	96.895	24.224	62.230
14d @ 59C	5	150.470	30.094	3.114
20d@52C	5	176.472	35.294	5.278

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	301.567	3	100.522	4.429	0.020	3.287
Within Groups	340.470	15	22.698			
Total	642.036	18				

ANOVA on Three Groups
SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	137.35	27.47	30.05
7d @ 58C	4	96.89	24.22	62.23
14d @ 59C	5	150.47	30.09	3.11

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	76.6	2	38.3	1.32	0.307	3.982
Within Groups	319.4	11	29.0			
Total	395.9	13				

ANOVAs on Two Groups
SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
7d @ 58C	4	96.9	24.2	62.23
14d @ 59C	5	150.5	30.1	3.11

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	76.6	1	76.6	2.69	0.145	5.591
Within Groups	199.1	7	28.4			
Total	275.7	8				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d@52C	5	176.47	35.29	5.28
14d@53C	4	176.77	44.19	70.95

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	175.9229085	1	175.9229	5.2635	0.0555	5.5914
Within Groups	233.9623097	7	33.4232			
Total	409.8852182	8				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	137.35	27.47	30.05
20d@52C	5	176.47	35.29	5.28

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	153	1	153.0422	8.6634	0.0186	5.3177
Within Groups	141	8	17.6653			
Total	294	9				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d@53C	4	176.8	44.2	70.9
14d @ 59C	5	150.5	30.1	3.11

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	442	1	442	13.7	0.00761	5.59
Within Groups	225	7	32.2			
Total	667	8				

Total Solids Destruction

TS redn	7d @ 58C	14d@53C	14d @ 59C	20d@52C	20d @ 67C
	15.770	29.030	34.346	28.862	48.488
	17.226	35.314	33.881	29.848	31.031
	14.922	33.996	35.425	33.374	28.675
	15.152	35.788	34.166	27.712	24.780
		35.984	34.300	31.382	29.429
Median	15	35	34	30	29
q1	15	34	34	29	29
min	15	29	34	28	25
max	17	36	35	33	48
q3	16	36	34	31	31

ANOVA on All Groups

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	162	32.5	85.4
7d @ 58C	4	63.1	15.8	1.07
14d @ 59C	5	172	34.4	0.346
20d@52C	5	151	30.2	4.89
14d@53C	5	170	34.0	8.39

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1020	4	255	12.1	0.0000457	2.90
Within Groups	399	19	21.0			
Total	1419	23				

ANOVA on Four Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d@53C	5	170	34.0	8.39
14d @ 59C	5	172	34.4	0.346
20d@52C	5	151	30.2	4.89
20d @ 67C	5	162	32.5	85.4

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>
Between Groups	54.0	3	18.0	0.728	0.550
Within Groups	396	16	24.7		
Total	450	19			

ANOVA on Two Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d@53C	5	170	34.0	8.39
14d @ 59C	5	172	34.4	0.346

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.402	1	0.402	0.0921	0.769	5.32
Within Groups	34.9	8	4.37			
Total	35.3	9				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d@52C	5	151	30.2	4.89
20d @ 67C	5	162	32.5	85.4

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	12.6	1	12.6	0.279	0.612	5.32
Within Groups	361	8	45.1			
Total	374	9				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d@53C	5	170.11	34.02	8.39
20d@52C	5	151.18	30.24	4.89

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	35.9	1	35.8528	5.3992	0.0486	5.3177
Within Groups	53.1	8	6.6404			
Total	89.0	9				

Appendix C: Other Standard Liquid Parameters

Ammonia

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	1200		1360	890	1010
	1250	970	1200	930	930
	1360	1010	970	1300	1050
	1100	1670	1010	1300	1300
	1300	1010	1250	1360	1200
	1250	720	1410	1150	1300
Median	1250	1010	1225	1225	1125
q1	1250	970	1058	985	1020
min	1100	720	970	890	930
max	1360	1670	1410	1360	1300
q3	1300	1010	1332.5	1300	1275

ANOVA

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	6	7460	1243	7867
7d @ 58C	5	5380	1076	124880
14d @ 59C	6	7200	1200	32240
20d@52C	6	6930	1155	40990
14d@53C	6	6790	1132	24697

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	91017	4	22754	0.531	0.714	2.776
Within Groups	1028487	24	42854			
Total	1119503	28				

Alkalinity

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	277	160	140	126	140
	290	173	146	130	130
	305	136	142	136	109
	270	129	146	138	106
	245	131	126	136	110
	198	108	116	120	112
Median	274	134	141	133	111
q1	251	130	130	127	109
min	198	108	116	120	106
max	305	173	146	138	140
q3	287	154	145	136	126

ANOVA

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	6	1585	264	1456
7d @ 58C	6	837	139.5	546
14d @ 59C	6	816	136	150
20d@52C	6	786	131	49.2
14d@53C	6	707	118	191

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	86637	4	21659	45.28	0.0000000000423	2.76
Within Groups	11959	25	478			
Total	98596	29				

ANOVA on Four Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
7d @ 58C	6	837	140	546
14d @ 59C	6	816	136	150
20d@52C	6	786	131	49
14d@53C	6	707	118	191

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1624	3	541	2.31	0.107	3.10
Within Groups	4680	20	234			
Total	6304	23				

ANOVA on Two Groups

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	6	816	136	150
14d@53C	6	707	118	191

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	990	1	990	5.81	0.0367	4.96
Within Groups	1705	10	170			
Total	2695	11				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d@52C	6	786	131	49.2
14d@53C	6	707	118	191

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	520	1	520	4.34	0.0639	4.96
Within Groups	1199	10	120			
Total	1719	11				

pH

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	7.67	7.15	6.86	7.68	7.94
	8.17	7.2	7.53	7.55	8.18
	8.2	7.4	7.42	7.55	6.99
	8.37	7.67	7.36	7.57	6.77
	8.25	7.48	7.18	7.67	6.4
	8.04	7.01	7.14	7.62	6.93
Median	8.2	7.3	7.3	7.6	7.0
q1	8.2	7.2	7.2	7.6	6.8
min	8.0	7.0	6.9	7.6	6.4
max	8.4	7.7	7.5	7.7	8.2
q3	8.3	7.5	7.4	7.7	7.7

ANOVA

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	6	48.7	8.12	0.0594
7d @ 58C	6	43.9	7.32	0.0588
14d @ 59C	6	43.5	7.25	0.0577
20d@52C	6	45.6	7.61	0.0035
14d@53C	6	43.2	7.20	0.4900

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.46	4	0.865	6.47	0.00103	2.76
Within Groups	3.35	25	0.134			
Total	6.81	29				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
7d @ 58C	6	43.9	7.32	0.0588
14d @ 59C	6	43.5	7.25	0.0577
20d@52C	6	45.6	7.61	0.0035
14d@53C	6	43.2	7.20	0.4900

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.594	3	0.198	1.30	0.302	3.10
Within Groups	3.05	20	0.152			
Total	3.64	23				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	6	43.5	7.25	0.0577
14d@53C	6	43.2	7.20	0.4900

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.00653	1	0.00653	0.0239	0.880	4.96
Within Groups	2.74	10	0.274			
Total	2.74	11				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d@52C	6	45.6	7.61	0.00347
14d@53C	6	43.2	7.20	0.4900

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.4921	1	0.492	1.99	0.188	4.96
Within Groups	2.47	10	0.247			
Total	2.96	11				

ORP

ORP	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	-463	-459	-483	-505	-491
	-464	-463	-478	-509	-490
	-461	-467	-478	-514	-487
	-459	-462	-483	-513	-487
	-458	-468	-491	-511	-485
	-460			-509	
	-460			-504	
	-461			-497	
	-459				
	-453			-485	
	-452				
	-451				
	-449				
	-449				
	-455				
	-454				
	-455				
	-458				
	-454				
Median	-458	-463	-483	-509	-487
q1	-460	-467	-483	-511	-490
min	-464	-468	-491	-514	-491
max	-449	-459	-478	-485	-485
q3	-454	-462	-478	-504	-487

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	19	-8676	-457	19.3
7d @ 58C	5	-2319	-464	14.3
14d @ 59C	5	-2414	-483	28.1
20d@52C	9	-4547	-505	82.4
14d@53C	5	-2440	-488	5.18

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	16386	4	4097	130	1.24E-21	2.62
Within Groups	1196	38	31.5			
Total	17582	42				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	19	-8676	-457	19.3
7d @ 58C	5	-2319	-464	14.3
14d @ 59C	5	-2414	-483	28.1
14d@53C	5	-2440	-488	5.18

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	5531	3	1844	103	6.89E-16	2.92
Within Groups	537	30	17.9			
Total	6068	33				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	5	-2414	-483	28.1
14d@53C	5	-2440	-488	5.18

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	72.2	1	72.2	4.34	0.0707	5.32
Within Groups	133	8	16.6			
Total	205	9				

Appendix D: Protein, Carbohydrate, and Fat Data

Protein

Protein Content of Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.9	1.3	1.1	1.3	1.5
	1.3	1.7	1.2	1.3	1.4
	1.6	1.3	1.6	1.4	1.4
	1.4	0.9	2.05	1.25	1.2
	1.2	1	2.6	1.2	1.15
					1.3
Median	1.3	1.3	1.6	1.3	1.4
q1	1.2	1.0	1.2	1.3	1.2
min	0.9	0.9	1.1	1.2	1.2
max	1.6	1.7	2.6	1.4	1.5
q3	1.4	1.3	2.1	1.3	1.4

ANOVA on Test Reactor Data

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	6.4	1.28	0.067
7d @ 58C	5	6.2	1.24	0.098
14d @ 59C	6	10.6	1.77	0.499
20d@52C	6	7.7	1.28	0.00567
14d@53C	7	9.1	1.3	0.02

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.15	4	0.286	2.08	0.115	2.78
Within Groups	3.30	24	0.138			
Total	4.45	28				

ANOVA on Crude Data

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	6.9	1.38	0.142
7d @ 58C	5	5.1	1.02	0.037
14d @ 59C	5	4.85	0.97	0.012
20d@52C	4	4.15	1.04	0.0823
14d@53C	6	7.3	1.22	0.210

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.580	4	0.145	1.41	0.267	2.87
Within Groups	2.06	20	0.103			
Total	2.64	24				

ANOVA on Tricling Fiter Activated Sludge Data

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	7.8	1.56	0.223
7d @ 58C	4	6.8	1.7	1.09
14d @ 59C	5	8.8	1.76	0.538
20d@52C	4	10.1	2.51	0.000625
14d@53C	6	12.7	2.11	0.354

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	2.59	4	0.647	1.52	0.236	2.90
Within Groups	8.08	19	0.425			
Total	10.7	23				

Carbohydrates

Carbohydrate Content of Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.8	0	1.2	0.7	0.8
	0.7	0.6	1	0.7	0.8
	0.6	0.9	0	0.6	1
	0.6	0	0.3	0.8	1
	0.5	0		0.9	0.8
					0.6
Median	0.6	0.0	0.7	0.7	0.8
q1	0.6	0.0	0.2	0.7	0.8
min	0.5	0.0	0.0	0.6	0.6
max	0.8	0.9	1.2	0.9	1.0
q3	0.7	0.6	1.1	0.8	1.0

ANOVA on Test Reactor Data

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	3.2	0.64	0.013
7d @ 58C	5	1.5	0.3	0.18
14d @ 59C	4	2.5	0.625	0.3225
20d@52C	5	3.7	0.74	0.013
14d@53C	6	5	0.833	0.0227

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.853	4	0.213	2.24	0.101	2.87
Within Groups	1.90	20	0.0952			
Total	2.76	24				

ANOVA on Crude Sludge Data

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	8.1	1.62	0.552
7d @ 58C	5	11	2.2	0.285
14d @ 59C	5	14.25	2.85	0.512
20d@52C	4	9.7	2.425	0.0292
14d@53C	6	14.05	2.34	0.298

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	3.94	4	0.985	2.82	0.0524	2.87
Within Groups	6.98	20	0.349			
Total	10.9	24				

ANOVA on Trickling Filter Activated Sludge

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	3.8	0.76	0.233
7d @ 58C	4	5.2	1.3	0.153
14d @ 59C	5	9.1	1.82	1.87
20d@52C	4	4.45	1.11	0.0140
14d@53C	6	6.6	1.1	0.308

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	3.02	4	0.754	1.37	0.281	2.90
Within Groups	10.4	19	0.550			
Total	13.5	23				

Fats

Fat Content of Test Reactor Sludge

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.6	0.6	0.5	0.4	0.6
	0.5	0.6	0.6	0.4	0.6
	0.5	0.5	0.5	0.4	0.5
	0.5	0.6	0.6	0.55	0.5
	0.5	0.6		0.6	0.5
					0.6
Median	0.5	0.6	0.55	0.4	0.55
q1	1	1	1	0	1
min	0.5	0.5	0.5	0.4	0.5
max	0.6	0.6	0.6	0.6	0.6
q3	0.5	0.6	0.6	0.55	0.6

ANOVA on Test Reactor Data

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	2.6	0.52	0.002
7d @ 58C	5	2.9	0.58	0.002
14d @ 59C	4	2.2	0.55	0.00333
20d@52C	5	2.35	0.47	0.0095
14d@53C	6	3.3	0.55	0.003

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0346	4	0.00865	2.19	0.107	2.87
Within Groups	0.079	20	0.00395			
Total	0.114	24				

ANOVA on Crude Sludge Data

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	5.6	1.12	0.037
7d @ 58C	5	4.1	0.82	0.002
14d @ 59C	5	4.9	0.98	0.007
20d@52C	4	3.4	0.85	0.0167
14d@53C	6	4.95	0.825	0.0338

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.342	4	0.0854	4.24	0.0120	2.87
Within Groups	0.403	20	0.0201			
Total	0.744	24				

ANOVA on Trickling Filter Activated Sludge Data

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
7d @ 58C	5	4.1	0.82	0.002
14d @ 59C	5	4.9	0.98	0.007
20d@52C	4	3.4	0.85	0.0167
14d@53C	6	4.95	0.825	0.0338

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.0866	3	0.0289	1.81	0.185	3.24
Within Groups	0.255	16	0.0159			
Total	0.341	19				

Appendix E: Gas Data

Hydrogen Sulphide

Corrected Concentration in Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	1.7	2.6	3.7	2.1	3.2
	0.0	0.7	0.0	4.9	0.0
	10.0	2.7	0.7	4.4	7.7
	0.0	1.4	0.7	0.6	7.7
	2.8	1.4	0.0	0.9	6.0
			1.8		0.6
Median	2	1	1	2	5
q1	0	1	0	1	1
min	0	1	0	1	0
max	10	3	4	5	8
q3	3	3	2	4	7

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	14.4	2.88	17.1
7d @ 58C	5	8.88	1.78	0.765
14d @ 59C	6	6.86	1.14	1.97
20d@52C	5	12.9	2.58	3.81
14d@53C	6	25.3	4.21	11.8

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	32.0	4	7.99	1.13	0.367	2.82
Within Groups	155	22	7.06			
Total	187	26				

ANOVA on First and Fourth Group

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	14.4	2.88	17.1
20d@52C	5	12.9	2.58	3.81

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.235	1	0.235	0.0226	0.884	5.32
Within Groups	83.5	8	10.4			
Total	83.7	9				

Corrected Concentration in Feed Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	35	20	25	15	15
	5	15	20	20	15
	5	35	20	25	
	70	32.5	20	15	25
	45	12.5	30	10	20
			20		20
Median	35	20	20	15	20
q1	5	15	20	15	15
min	5	12.5	20	10	15
max	70	35	30	25	25
q3	45	32.5	23.75	20	20

ANOVA on All Groups

SUMMARY

Groups	Count	Sum	Average	Variance
20d @ 67C	5	160	32	770
7d @ 58C	5	115	23	104
14d @ 59C	6	135	22.5	17.5
20d@52C	5	85	17	32.5
14d@53C	5	95	19	17.5

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	664	4	166	0.921	0.470	2.84
Within Groups	3785	21	180			
Total	4449	25				

Methyl Mercaptan

Corrected Concentration in Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	13.3	16.0	3.33	18.0	6.65
	3.33	33.3	3.33	13.3	
	27.9	20.0	6.65		13.4
	3.33	6.65	3.33	13.4	
	20.0	13.3	3.33		6.83
			3.33	3.42	
Median	13.3	16.0	3.33	13.4	6.83
q1	3.33	13.3	3.33	10.8	6.74
min	3.33	6.65	3.33	3.42	6.65
max	27.9	33.3	6.65	18.0	13.4
q3	20.0	20.0	3.33	14.6	10.1

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	67.8	13.6	114
7d @ 58C	5	89.1	17.8	97.8
14d @ 59C	6	23.3	3.88	1.84
20d@52C	4	48.1	12.0	37.7
14d@53C	3	26.9	8.97	15.0

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	586	4	147	2.64	0.0681	2.93
Within Groups	1000	18	55.6			
Total	1587	22				

ANOVA done on Last Two Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d@52C	4	48.1	12.0	37.7
14d@53C	3	26.9	8.97	15.0

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	16.1	1	16.1	0.562	0.487	6.61
Within Groups	143	5	28.6			
Total	159	6				

Corrected Concentration in Feed Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	42.6	53.2	39.9	7.56	11.6
	13.3	39.9	40.5	49.1	16.8
	26.6	39.9	23.9	20.7	
	59.9	66.5	59.9	19.9	29.3
	79.8	26.6	26.6		
			53.2		18.1
Median	42.6	39.9	40.2	20.3	17.4
q1	26.6	39.9	29.9	16.8	15.5
min	13.3	26.6	23.9	7.56	11.6
max	79.8	66.5	59.9	49.1	29.3
q3	59.9	53.2	50.0	27.8	20.9

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	222	44.4	695
7d @ 58C	5	226	45.2	230
14d @ 59C	6	244	40.7	201
20d@52C	4	97.3	24.3	308
14d@53C	4	75.8	18.9	55.7

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	2619	4	655	2.15	0.114	2.90
Within Groups	5795	19	305			
Total	8413	23				

Ammonia

Corrected Concentration in Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	96.2	92.9	72.2	4.88	109
	101	27.7	77.7	4.20	33.1
	35.3	12.0	230	7.56	1.05
	221	106	37.3	6.44	1.71
	84.0	40.3	44.8	8.60	0.00
			89.3		10.6
Median	96.2	40.3	74.9	6.44	6.17
q1	84.0	27.7	51.6	4.88	1.21
min	35.3	12.0	37.3	4.20	0
max	221	106	230	8.60	108.9
q3	101	92.9	86.4	7.56	27.495

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	538	108	4691
7d @ 58C	5	279	55.8	1717
14d @ 59C	6	551	91.8	4970
20d@52C	5	31.7	6.33	3.33
14d@53C	6	155	25.9	1810

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	38679	4	9670	3.57	0.0217	2.82
Within Groups	59541	22	2706			
Total	98219	26				

ANOVA Done on Two Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	538	108	4691
20d@52C	5	31.7	6.33	3.33

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	25594	1	25594	10.9	0.0108	5.32
Within Groups	18778	8	2347			
Total	44372	9				

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
14d @ 59C	6	551	91.8	4970
14d@53C	6	155	25.9	1810

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	13045	1	13045	3.85	0.0782	4.96
Within Groups	33896	10	3390			
Total	46941	11				

Corrected Concentration in Feed Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	1.24	1.29	1.99	0	0
	1.87	1.34	1.33	0	0
	0.00	0.00	1.36	0	0
	1.22	1.34	0.00	0	0
	1.28	0.00	0.00	0	0
			0.00		
Median	1.24	1.29	0.664	0	0
q1	1.22	0.00	0	0	0
min	0.00	0.00	0	0	0
max	1.87	1.34	1.99	0	0
q3	1.28	1.34	1.35	0	0

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	5.61	1.12	0.468
7d @ 58C	5	3.96	0.793	0.524
14d @ 59C	6	4.68	0.779	0.785
20d@52C	5	0	0	0
14d@53C	5	0	0	0

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	5.27	4	1.32	3.50	0.0242	2.84
Within Groups	7.89	21	0.376			
Total	13.2	25				

ANOVA on First Three Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	5.61	1.12	0.468
7d @ 58C	5	3.96	0.793	0.524
14d @ 59C	6	4.68	0.779	0.785

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.389	2	0.194	0.320	0.732	3.81
Within Groups	7.89	13	0.607			
Total	8.28	15				

Amines

Corrected Concentration in Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	174	165	156	13.8	161
	168	166	161	18.4	74.9
	80.3	70	166	19.2	67.2
	169	163	157	15.4	2.93
	170	162	164	15.6	0.998
			160		7.54
Median	169	163	160	15.6	37.4
q1	168	162	158	15.4	4.08
min	80.3	70	156	13.8	0.998
max	174	166	166	19.2	161
q3	170	165	163	18.4	73.0

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	761	152	1619
7d @ 58C	5	725	145	1761
14d @ 59C	6	962	160	15.6
20d@52C	5	82.4	16.5	5.02
14d@53C	6	314	52.3	3902

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	93345	4	23336	15.5	3.63E-06	2.82
Within Groups	33130	22	1506			
Total	126475	26				

ANOVA on First Three Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	761	152	1619
7d @ 58C	5	725	145	1761
14d @ 59C	6	962	160	15.6

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	650	2	325	0.311	0.738	3.81
Within Groups	13597	13	1046			
Total	14247	15				

Corrected Concentration in Feed Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	26.9	27.7	4.24	0	0
	5.42	2.84	2.86	0	0
	0	0	0	0	0
	2.66	2.84	2.85	0	2.99
	2.78	0	2.85	0	2.98
			4.25		12.4
Median	2.78	2.84	2.85	0	1.49
q1	2.66	0	2.85	0	0
min	0	0	0	0	0
max	26.9	27.7	4.25	0	12.4
q3	5.42	2.84	3.90	0	2.99

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	5	37.8	7.55	121
7d @ 58C	5	33.4	6.67	140
14d @ 59C	6	17.1	2.84	2.40
20d@52C	5	0.0	0.00	0
14d@53C	6	18.4	3.06	23.1

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	192	4	48.0	0.902	0.480	2.82
Within Groups	1171	22	53.2			
Total	1363	26				

Dimethyl Sulphide

Corrected Concentration in Test Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.3255	0.0705	0.048	0.048	0.048
	0.093	0.123	0.0505	0.168	0.048
	0.098	0.0605	0.048	0.048	0.048
		0.058	0.048	0.048	0.048
			0.048		0.048
			0.048		0.048
Median	0.098	0.0655	0.048	0.048	0.048
q1	0.0955	0.059875	0.048	0.048	0.048
min	0.093	0.058	0.048	0.048	0.048
max	0.3255	0.123	0.0505	0.168	0.048
q3	0.21175	0.083625	0.048	0.078	0.048

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	3	0.517	0.172	0.0176
7d @ 58C	4	0.312	0.0780	0.000929
14d @ 59C	6	0.291	0.0484	1.04E-06
20d@52C	4	0.312	0.078	0.0036
14d@53C	6	0.288	0.048	6.94E-19

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.0370	4	0.00925214	3.41	0.0305	2.93
Within Groups	0.0489	18	0.002715104			
Total	0.0859	22				

ANOVA on Last Four Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
7d @ 58C	4	0.312	0.078	0.000929
14d @ 59C	6	0.291	0.0484	1.04E-06
20d@52C	4	0.312	0.078	0.0036
14d@53C	6	0.288	0.048	6.94E-19

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.00426	3	0.00142	1.67	0.213	3.24
Within Groups	0.0136	16	0.000850			
Total	0.0179	19				

Corrected Concentration in Feed Reactor

	20d @ 67C	7d @ 58C	14d @ 59C	20d@52C	14d@53C
	0.469	0.477	0.497	0.354	0.354
	0.439	0.644	0.509	0.354	0.354
	0.604	0.497	0.509	0.354	0.354
		0.502	0.504		0.354
		0.497	0.354		0.354
			0.504		0.354
Median	0.469	0.497	0.504	0.354	0.354
q1	0.454	0.497	0.498	0.354	0.354
min	0.439	0.477	0.354	0.354	0.354
max	0.604	0.644	0.509	0.354	0.354
q3	0.537	0.502	0.508	0.354	0.354

ANOVA on All Groups

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
20d @ 67C	3	1.51	0.504	0.00772
7d @ 58C	5	2.62	0.523	0.00467
14d @ 59C	6	2.88	0.479	0.00380
20d@52C	3	1.06	0.354	2.78E-17
14d@53C	6	2.12	0.354	0

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	0.122	4	0.0306	10.4	0.000155	2.93
Within Groups	0.0531	18	0.00295			
Total	0.176	22				