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**The Effect of Aerobic Biological Treatment
on Hydrogen Sulfide Emissions**

by

Linh Ly

**A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree**

Western Michigan University

Kalamazoo, Michigan

April 17, 1997

ABSTRACT

Sulfides from Kraft mills and other processes are an odor problem. Using Thiobacillus thiooxidans as bacteria to be inoculated into an aerobic biological reactor can be an alternative to reducing the quantity and improving the quality of effluent gases. Approximately, two to three months was needed to insure that the Thiobacillus thiooxidans were growing in chains and colonies. So, this thesis was not fully completed due to the fact that the bacteria did not have enough time to grow. No conclusion can be made on the feasibility of using an aerobic biological reactor with an inert packing to degrade or eliminate odorous gases such as hydrogen sulfides. The Kitagawa Precision tubes proved to be a good and easy method for analyzing the concentration of hydrogen sulfides (inlet or exit).

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INTRODUCTION

Although the paper industry has cleaned up it's image with respect to gaseous emissions in recent years, we are still responsible for an offensive air pollutant. The biggest producer of hydrogen sulfide and reduced sulfur compounds comes from the Kraft mill pulping process (Refer to Figure I). Kraft mill odor is principally due to four reduced sulfur gases (total reduced sulfur emissions): hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Some characteristics of the individual gases are given in Figure II. The major sources of total reduced sulfur emissions are digester blow and relief gases, multiple effect evaporator noncondensibles, and recovery boiler exhaust gases. Measurable concentrations are also found in the brown stock washer and seal tank vents, liquor storage vents, smelt dissolving tank vent, lime kiln exhaust, black liquor oxidation exhaust, and slaker exhaust. (1, pgs. 392-393) The Kraft operations involves a digestion process that can either be batch or continuous. In batch cooking, the digester vessel is filled with chips and enough liquor is added to cover the chips. The contents are then heated usually by forced circulation of the cooking liquor through a heat exchanger. Air and other noncondensable gases are relieved through a pressure control valve at the top of the vessel. In continuous cooking, the chips are first carried through a steaming vessel where air and other noncondensibles

are purged. The recovery of chemicals and energy from the residual black liquor and reconstitution of the recovered chemicals to form white liquor are important parts to the kraft mill operation. The weak black liquor from the brown stock washers is processed through the following steps: a series of evaporation and chemical addition steps into heavy black liquor, incineration of heavy black liquor in the recovery furnace to form inorganic smelt, dissolving of furnace smelt in water to form green liquor, and causticizing of green liquor with reburned lime to form white liquor for the next cooking cycle. The function of the recovery furnace is to chemically reduce the oxidized sulfur compounds contained in the burning solids to sulfide. (1, pgs. 76-77)

Typical reduced sulfur gas emission rates from Kraft pulp mill sources are shown in Table I and II. (2, pg. 1-6) The noncondensable gases from digesters and evaporators are small-volume, high concentration sources, and are usually treated by incineration. The high volume recovery furnace gases are more difficult to treat, and best results are achieved by reducing emissions at the source by such means as black liquor oxidation, low-odor recovery boiler design, and proper operation of the recovery boiler. (1, pgs. 393-394)

The approximate odor threshold for these reduced sulfur gases are listed in Table III. Hydrogen sulfides has an extremely high acute toxicity and has caused many deaths both in the workplace and in areas of natural accumulation. Hydrogen sulfides can be hazardous because brief exposure to hydrogen

sulfide at a concentration of 140 mg/m³ causes conjunctivitis and keratitis (eye damage), and exposures at above 280 mg/m³ causes unconsciousness, respiratory paralysis, and death (Refer to Table IV). There is no evidence of adverse health effects from repeated long-term exposure to hydrogen sulfide at low concentrations, although there is some evidence pointing to nervous-system, cardiovascular, gastrointestinal, and ocular disorders. Symptoms of low level exposure can include headache, nausea, insomnia, fatigue, and inflammation of the eyes and mucous membranes. Irritation of the eyes and respiratory system has been reported at concentrations below 1 ppm. Hydrogen sulfide can have a deceptively sweet smell at 30-100 ppm and it can deaden the sense of smell above this range. Occupational Health and Safety Administration's acceptable ceiling concentration is 20 ppm. (3, pg. 120)

The relevance of this thesis is that in recent years there has been an increasing amount of concern regarding air pollution. To limit the gas emissions, the Environmental Protection Agency has set regulations to manage the air pollution problem. The aerobic biological reactor is a possible alternative to eliminate odorous gases such as reduced sulfur compounds. It can also be a less expensive alternative to conventional air treatment.

THEORETICAL AND BACKGROUND DISCUSSION

A literature survey focusing on biological treatment of odorous gas using Thiobacillus revealed many sources. The Thiobacillus genus is a colorless sulfur bacteria comprised of very heterogeneous organisms which share the ability to oxidize, reduce, or partially oxidize inorganic sulfur. They are also Gram negative aerobes and chemolithotrophic (obligate or facultative) and can be found wherever reduced sulfur compounds are available (e.g., in sediments, soil, at aerobic/anaerobic interfaces in water, etc.). They appear rod-shaped (~0.5 x 1.0-4.0 um) with some species motile by means of a single polar flagellum. No resting stages are known. Energy is derived from the oxidation of one or more reduced sulfur compounds, including sulfides, sulfur, thiosulfate, polythionates, and thiocyanate. Sulfate is the end product of sulfur compound oxidation, but sulfur, sulfite, or polythionates may be accumulated by most species. All species can fix carbon dioxide and are capable of autotrophic growth. Some species are obligately chemolithotrophic while others are also able to grow chemoorganotrophically. This genus includes obligate aerobes and facultative denitrifying types, and its species exhibit pH optima of 2-8 with temperature optima of 20-43°C. (4, pgs. 427, 429, 436)

The Thiobacillus genus can be used for many purposes. One of which is to treat sulfide-containing effluents by

biologically oxidizing the effluents to sulfate. Conversion of sulfide to elemental sulfur could be an interesting alternative treatment process, because it allows the removal of solid sulfur, resulting in a decrease in the total sulfur content of waste water. Sulfur formation by the *Thiobacillus* was studied in aerobic, substrate-limited continuous cultures. The performance of transient-state and steady-state cultures was compared. Below a dilution rate of 0.3 h^{-1} , sulfate-producing steady states were obtained and cultures grown with sulfide or thiosulfate showed similar characteristics (e.g. cell yields, oxidation capacities, and CO_2 fixation capacities). Elemental sulfur was a major product about the dilution rate, but steady states were difficult to achieve, because of adherence of sulfur to the fermentor surfaces and the accumulation of sulfide. These problems could be bypassed using transient-state experiments of one hour. It was then found that elemental sulfur was formed under oxygen limitation or at high substrate loads. Sulfide and thiosulfate proved to be equivalent substrates for the *Thiobacillus*. It was then concluded that transient-state cultures of *Thiobacilli*, pregrown as sulfate-producing steady-state cultures, provide experimental conditions for the quantitative assessment of sulfur formation from sulfide and from thiosulfate. (5, pgs. 170-171)

Thiobacillus ferrooxidans was another source of bacteria that was used to oxidize reduced sulfur compounds and inorganic iron. Most recently, with the heightened awareness

of environmental problems with the use of high-sulfur coals and the recovery of precious metals from pyrite-rich ores, mining and coal companies have displayed interests in the use of *Thiobacillus ferrooxidans* as a biological solution to coal desulfurization and ore bioleaching processes. *Ferrooxidans* were obtained from the American Type Culture Collection and was purified by four successive isolations of individual colonies from plates containing solidified medium. Growth was conducted with FeSO_4 based medium. (6, pgs. 2-3)

The specific species that will be dealt with in this thesis are *Thiobacillus thiooxidans*. *Thiobacillus thiooxidans* are an acidophilic chemoautotrophic bacterium that uses elemental sulfur or reduced sulfur compounds as substrates at temperatures up to about 40°C and pH values as low as 0.5. This sulfur-oxidizing bacterium plays a major role in the cycling of sulfur in the biosphere. The ability of microorganisms to oxidize inorganic sulfur can be applied to the bioleaching of base and precious metals from various minerals and to the removal of pyritic sulfur (FeS_2) from coal (desulfurization). The growth kinetics of *Thiobacillus thiooxidans* on elemental sulfur in batch cultures at 30°C and pH 1.5 was studied by measuring the time courses of the concentration of adsorbed cells on sulfur, the concentration of free cells suspended in liquid medium, and the amount of sulfur oxidized. As the elemental sulfur was oxidized to sulfate ions, the surface concentration of adsorbed cells per unit mass of sulfur approached a maximum value (maximum

adsorption capacity of sulfur particles) whereas the concentration of free cells continued to increase with time. There was a close relationship between the concentrations of free and adsorbed cells during the microbial sulfur oxidation. The total concentration of free and adsorbed cells increased in parallel with the amount of sulfate formed. The total growth on elemental sulfur gave a characteristic growth curve in which a linear-growth phase followed the period of an initial exponential phase. The batch rate data collected under a wide variety of inoculum levels (about 10^5 to 10^8 cells per mL) were consistent with a kinetic model assuming that the growth rate of adsorbed bacteria is proportional to the product of the concentration of adsorbed cells and the fraction of adsorption sites unoccupied by cells. (7, pgs. 3618-3618)

The *Thiobacillus* genus (*T. thioparus*) can also be used to treat wastewaters and remove H_2S from a gas that is bubbled through the culture. Mixed cultures of bacteria from the *Beggiatoa* and *Thiothrix* genera have also been utilized in a similar manner. *Thiobacillus ferrooxidans* have been used as the basis of gas treatment processes in which H_2S was first precipitated as CuS or FeS . It has been demonstrated that *T. denitrificans* may be cultured aerobically or anaerobically in batch and continuous reactors on $H_2S(g)$ under sulfide-limiting conditions. The aerobic growth of *T. denitrificans* in the presence of floc-forming heterotrophs produced a H_2S active floc with excellent settling characteristics. Batch growth

of other Thiobacilli on $\text{H}_2\text{S}(\text{g})$ as an energy source was investigated using a B. Braun Biostat M bench-scale fermentor. In each batch experiment, each organism was first grown in thiosulfate medium at the temperature and pH given by the American Type Culture Collection (ATCC). The medium contains thiosulfate as an energy source, ammonium chloride as a source of reduced nitrogen, NaHCO_3 as a source of carbon, a phosphate buffer, MgSO_4 , and trace minerals. Aeration was provided at a rate that maintained 60–100 μm of oxygen. Each reactor was autoclaved at 121°C and 205 kPa for 30 minutes prior to inoculation with 20 mL of the stock culture. In early batch experiments, cells were grown on thiosulfate until the thiosulfate was depleted before introducing $\text{H}_2\text{S}(\text{g})$. In later experiments, cells were harvested by centrifugation, washed, and resuspended in fresh medium without thiosulfate prior to the initiation of an H_2S feed. The purpose of the medium change was to eliminate sulfate produced by thiosulfate oxidation so the sulfate produced from H_2S oxidation could be more accurately quantitated. *T. thioparus* was observed to produce elemental sulfur when grown on thiosulfate as an energy source. The cells and sulfur were observed to agglomerate and accumulate at the air/liquid interface. None of the other Thiobacilli were observed to produce elemental sulfur when grown on thiosulfate but exhibited lower biomass yields and lower NH_4^+ utilization. (8, pgs. 1150–1154)

The design idea for the aerobic biological reactor came from an article written by Kiared, Bibeau, and Brzezinski. A biofiltration process was originally developed for the odor abatement of waste gases was proven to be an effective and an inexpensive method for the removal of volatile organic compounds (VOC). The technique was based on the ability of micro-organisms (bacteria) to convert, under aerobic conditions, organic pollutants to water, carbon dioxide, and biomass. The biofilter was a PVC column with a diameter of 0.15 meters and a height of 1.20 meters (Refer to Table V). The column was filled with a humidified and conditioned and sieved granules of peat supported at the bottom by a perforated sieve plate. Polystyrene particles were placed in the bottom of the column in order to distribute the gas before entering the filter bed. The packing was inoculated with a specific micro-organism. The nutrient solution (mainly Na_2HPO_4 , KH_2PO_4 , NH_4Cl) was pumped over the support material to maintain the layer of water to supply the micro-organisms with nutrients and to prevent drying out of the filter and the loss of biological activity. Contaminated air flowed upwards through the peat bed and cleaned air was evacuated at the top of the column. To keep the moisture content of the filter bed at a desired level between 50%-70%, inflowing gas was saturated with water in a separate humidification column outside the filter bed (Refer to Figure III). Flow rates were measured by volumetric flow meters, the relative humidity of the air was measured at the entrance

of the biofilter with a humidity sensor that also measured the inlet air temperature. The feed to the biofilter was a synthetic waste gas containing between 200 and 1000 ppm of ethanol or toluene. After a period of acclimatization (one week), the performance of the unit could be assessed. During one month of experimentation, the conversion of ethanol remained around 80%. The toluene conversion had a direct relation with the humidity content of the peat. It was concluded that the peat offered a favorable life environment for the micro-organism, at the moisture level investigated. The pH of the medium was stable around neutral (pH = 7). No acid intermediates were produced and the pressure drop (measured daily by a liquid differential manometer) was also minimal. Good performance was obtained for the removal efficiency and elimination capacity for ethanol and toluene. The bacteria used maintained a good level of activity even under local dryness conditions. (9, pgs. 148-149)

EXPERIMENTAL

The first step in this thesis project was to obtain a mixture of hydrogen sulfide and air.

Hydrogen Sulfide and Air

The hydrogen sulfide and air mixture will be used for the *Thiobacillus thiooxidans* to grow on.

- Materials:

- a. Aquarium pump (air source)
- b. 55 gallon polyethylene form fitting bag with injection port
- c. 55 gallon fiber barrel drum with lid
- d. Tubing: Tygon
- f. Hydrogen sulfide gas (provided by Chemistry Department)

- Procedure:

Initially, air was pumped from the aquarium pump to the polyethylene bag filling it up to approximately 50 gallons. Next, ten milliliters (mL) of hydrogen sulfide was injected into the bag through an injection port. Then, the hose from the aquarium pump was reattached to the injection port, pushing air through to make sure all hydrogen sulfide was injected. From this mixture, the concentration should be approximately 50 parts per million (50 ppm).

10 mL of H₂S

50 gallons of air X $\frac{3.785 \text{ L}}{1 \text{ gal}}$ X $\frac{1000 \text{ mL}}{1 \text{ L}}$ = 189250 mL of air

Concentration = $\frac{10 \text{ mL of hydrogen sulfide}}{189250 \text{ mL of air}}$ = 0.00005284

= 0.00005284 x 10⁶ = 52.84 ppm

Thiobacillus Thiooxidans

The *Thiobacillus thiooxidans* will be used to oxidize the H₂S.

- Materials:

- a. American Type Culture Collection (ATCC) *Thiobacillus thiooxidans* # 19377
- b. Medium 125
- c. 500 mL Erlenmeyer flask with side arm

- Procedure:

The first step was to prepare the medium (salt solution) following the information provided by ATCC for the stock culture:

$(\text{NH}_4)_2\text{SO}_4$	0.2 grams
MgSO_4	0.5 grams
CaCl_2	0.25 grams
KH_2PO_4	3.0 grams
FeSO_4	5.0 milligrams
Tap water	1.0 liters

Instead of using 1.0 L of tap water use 500 mL of distilled water. Prepare the salt solution and carefully pour 250 ml down the side of the flask. Next, inject 1 mL of inoculant into salt solution.

Flask Apparatus Setup

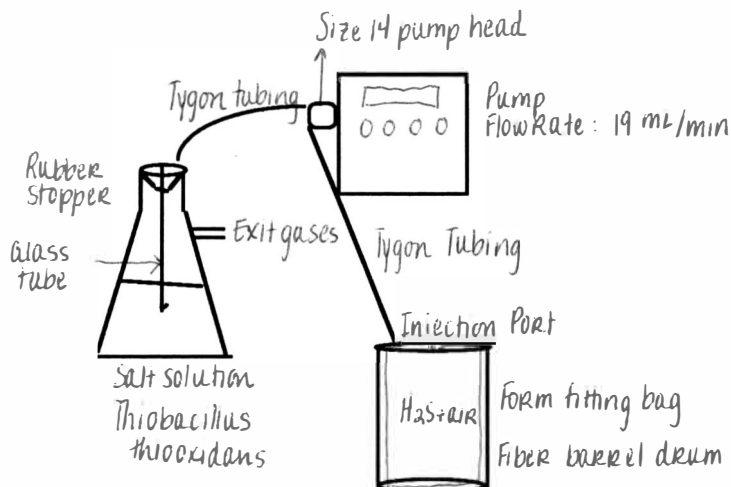
The hydrogen sulfide and air mixture will bubble through the culture for the *T. thiooxidans* to grow on.

- Materials:

- 500 mL side arm Erlenmeyer flask
- Tubing: Tygon
- Glass tube
- Peristaltic pump
- Hydrogen sulfide and air mixture

- Procedure:

Set up apparatus according to diagram below.



Run the flask apparatus under a hood at about 26°C for approximately two to three months making sure that the *Thiobacillus thiooxidans* are growing (check by Gram stain). Make sure to refill polyethylene bag with hydrogen sulfide and air when bag runs out following previous procedure.

Bacteria Staining (Gram stain)

Gram staining attempts to identify bacteria in a solution.

- Materials:

- a. Gram staining solutions:
 - Hucker's Crystal violet
 - Gram's Iodine
 - 95% Ethyl alcohol
 - 0.25% Safranin
- b. Slides
- c. Microscope
- d. Heat flame

- Procedure:

Take a sample of solution out of the flask and place onto the slide. Next, let the slide air dry. Then, run slide through heat flame at least three times to make sure everything is sterile. Stain the slide as follows:

- a. Flood the crystal violet for one minute
- b. Pour off excess dye and wash gently in tap water and drain the slide against a paper towel
- c. Flood the smears with Gram's iodine for one minute
- d. Wash with tap water and drain carefully. (Do not blot)
- e. Wash with 95% alcohol for 15–20 seconds or drip onto slide held at slight angle until blue color stops coming out of smear
- f. Wash with tap water at the end of the 30 seconds to stop the decolorization. Drain.
- g. Counterstain with 0.25% safranin for 30 seconds
- h. Wash, drain, and blot
- i. Place under microscope

Since *Thiobacillus thiooxidans* are Gram negative bacteria, they will look rod-shaped with two connected to each other. They also grow in chains or colonies.

Reference: Microbiology Department

Aerobic Biological Reactor Setup

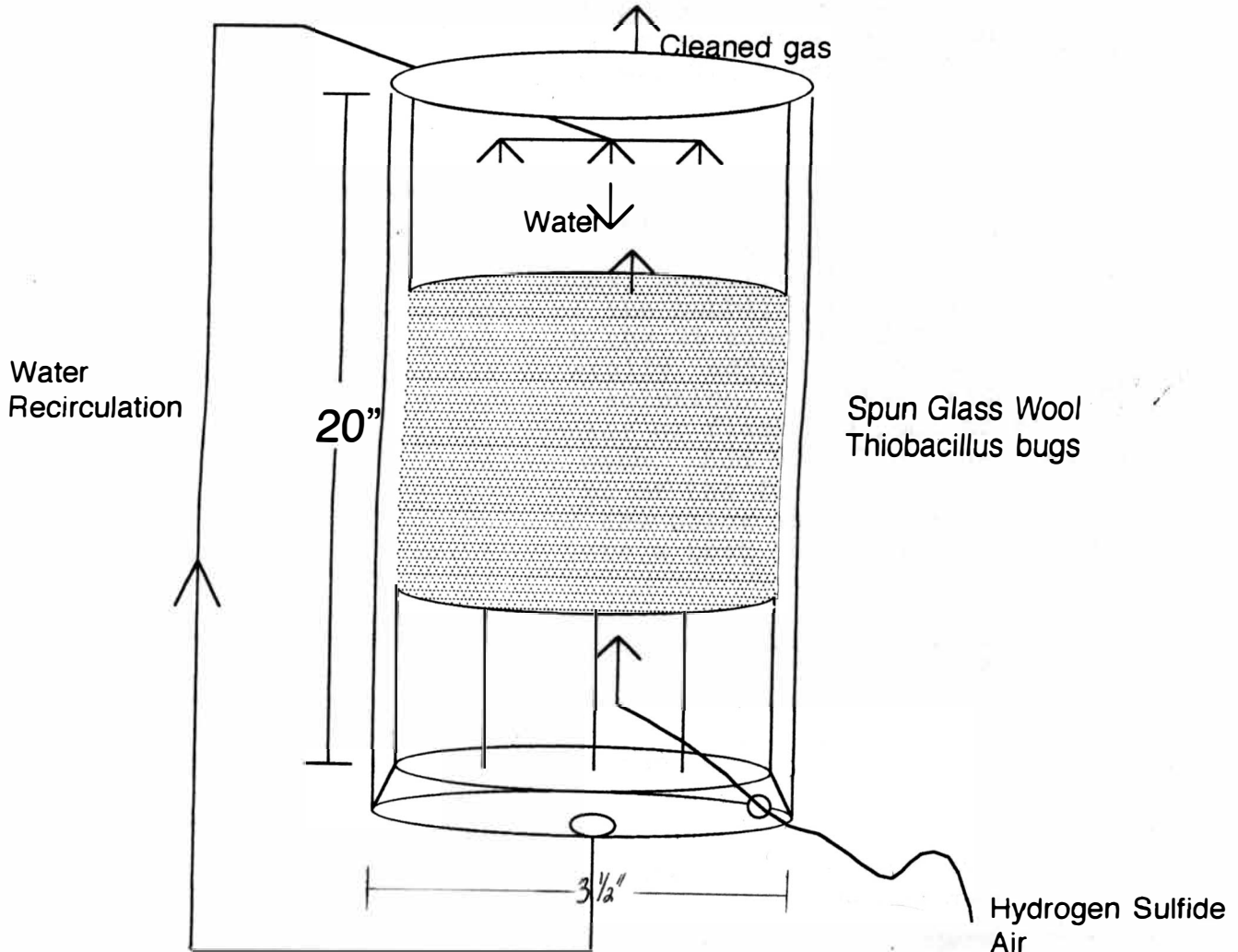
- Materials:

- a. Clear piping: 3 1/2 inch diameter by 20 inches tall
- b. Wooded base with injection port and drainage hole

- c. Spun glass wool
- d. Perforated plate
- e. *Thiobacillus thiooxidans*
- f. Hydrogen sulfide and air mixture
- g. Peristaltic pump

- Procedure:

Set up reactor according to diagram.



Gas Analysis

There was two methods in which the gas was analyzed. The first was the methylene blue and the second was done using the Kitagawa detection tubes.

- Methylene blue

Reagents

- a. Stock Zinc Acetate Solution, 20%. Dissolve 200 grams of C.P. zinc acetate in 1 liter of distilled water.

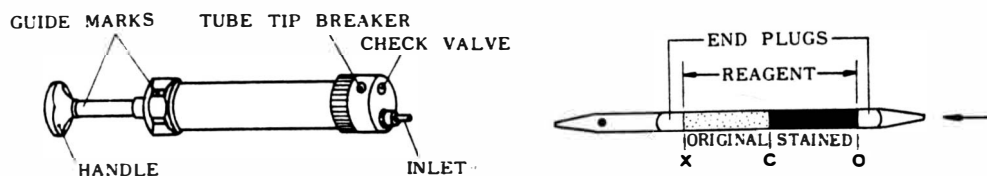
- b. Dilute Zinc Acetate Solution, 2%. Dilute 100 mL of the stock solution to 1 liter with distilled water and acidity with about three drops acetic acid.
- c. Diamine Reagent. Dissolve 0.15 grams p-amino-N,N-dimethylaniline sulfate in a cooled mixture of 100 mL concentrated sulfuric acid and 50 mL distilled water.
- d. Ferric Chloride Solution. Dissolve 2.7 grams $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in 50 mL concentrated hydrochloric acid and dilute to 100 mL with distilled water.
- e. Iodine Solution. 0.1 N I, standardized solution.
- f. Sodium Thiosulfate Solution, 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ standardized solution.

Procedure

Bubble the gas sample (inlet or exit) into 50 mL of the 2% zinc acetate solution contained in a wide mouth bottle until a faint turbidity forms, measuring the volume of gas used. Wash the contents of the bubbling bottle into a 1 liter volumetric flask with the 2% zinc acetate solution, rinsing out the bottle carefully, adjust the volume to 1000 mL with the 2% zinc acetate solution, and mix. Pipet 50 mL of this solution into a beaker or flask and cool to at least 10°C in an ice-water bath. Add 5.0 ml of the diamine reagent, stir, and add 1.0 mL of the ferric chloride solution. Stir and measure the color after standing 15-30 min. Place this solution into a test tube and measure in the Spec-20.

Reference: Boltz, D., Colorimetric Determination of Nonmetals, New York Interscience: 1958, pgs. 280-285.

• Kitagawa Precision Gas Detection



Sampling:

1. Cut tips off a fresh detector tube by bending each tube end in the tube tip breaker.
2. Insert the tube tip, marked with red dot, securely into the pump inlet.
3. Make certain the pump handle is all the way in. Align the guide marks on the shaft and back plate of the pump.

4. Pull the handle all the way out. Rock it with a half turn. Wait 3 minutes.
5. Unlock the pump handle by making a half turn back. If the handle retracts by more than 5 mL (about 1/4"), this means that a particle is lodged in the constant flow orifice and is obstructing the fixed flow rate, causing erroneous results.

Measurement:

1. When sampling is completed, remove the detector tube from the pump inlet.
2. Place the tube vertically against the concentration chart with stained end down.
3. Position top "X" and bottom "O" boundaries reagent and end plugs on the lines "X-X" and "O-O" respectively.
4. Read concentration by the length of stain "O-C" (Refer to Figure IV).

Reference: Kitagawa Precision Gas Detector

RESULTS AND DISCUSSION

Initially, the hydrogen sulfide and air mixture was diluted to a concentration of approximately 30 parts per million (ppm). The *Thiobacillus thiooxidans* was inoculated in the medium using the directions provided by ATCC. Five hundred milliliters (mL) of distilled water was used instead of one liter (L) resulting in a double quantity of salt solution to water. Next, two hundred and fifty milliliters of the salt solution was poured into the flask and one milliliter of the *T. thiooxidans* was injected. Then, the hydrogen sulfide and air mixture was bubbled into the flask using the apparatus described in the experimental using a flow rate of 19 mL per minute. No bacteria growth was noticed. Four more milliliters of H₂S was added to the polystyrene bag resulting in a concentration of 50 ppm (which was above the acceptable repeated exposure level). Apparatus ran for three more days without any sight of bug growth. Sulfur granules were added to the flask to give additional nutrients to bugs, still no bacteria activity was observed. It was concluded that not enough of the hydrogen sulfide was being bubbled into the flask apparatus.

Preliminary testing with methylene blue and precision tubes were performed to observe the accuracy of the methods. Refer to Table VI for the results. The polystyrene bag contained a known concentration of approximately 50 ppm. The first volume of gas injected into the 2% zinc acetate was 6 mL, resulting in an absorbance of 0.79%. The second volume

of gas used was 12 mL, resulting in an absorbance that was hardly noticeable. The final volume injected was 18 mL, resulting in an absorbance of 1.3%. None of the volumes used caused a faint turbidity to form. It was concluded that the methylene blue method did not produce repeatable results. Kitagawa precision tubes were also used to determine the concentration within the bag. Refer to Table VII for these results. Test one resulted in a concentration of 25 ppm while the second test was 6 ppm. These results may not be correct due to reading the concentration chart erroneously.

A new medium solution was made using 200 mL of salt solution with 1 mL of inoculant. The solution appeared cloudy that may have been a result of the salts settling. The concentration of H₂S and air was increased from 50 ppm to 85 ppm. A dual apparatus was set up for the original flask with sulfur granules and the new flask with the same amount of H₂S and air being bubbled through each. A sample of solution from the new flask was observed under a microscope. Clusters of filament looking items (salt solution settling) were noticed but no bacteria was growing. It was then concluded that not enough H₂S was being used or else the hydrogen sulfide provided from the Chemistry Department was not 99% pure. There was still no growth in the sulfur granule flask.

Another bag of H₂S and air was made up with a concentration of 50 ppm. The Kitagawa precision tubes were used again to determine the concentration within the bag.

Two Kitagawa tubes were used, one old and one new. The old Kitagawa tube resulted in a concentration reading of 50 to 100 ppm. The new tube resulted in a reading of 40 to 50 ppm, concluding that the H₂S was 99% pure. An explanation for no bacteria growth could have been a result of absorption of the H₂S gas into the Tygon tubing. The concentration coming out of the Tygon tubing was also tested with a Kitagawa tube. There was approximately 35 ppm concluding that there was some absorption, but the concentration was still high enough for the bacteria to grow because only a concentration of 10 ppm was needed. Since, the amount of the concentration of H₂S going into the flask exceeded the amount needed, there was no reason for the bacteria to not grow. So, the exit gas coming out of the side arm of the flask was also tested, no concentration of H₂S was observed, inferring that all of the H₂S was being absorbed into the salt solution. The original test tube from ATCC, the sulfur granule flask, and the new flask were Gram stained for the presence of bacteria. The original test tube had a few *T. thiooxidans*. The new flask also had a few bacteria with some in chains (Refer to Figure V), resulting in the conclusion that the bacterias were growing but very slowly. A longer amount of time (a couple of more weeks) was needed before they could be used in the aerobic biological reactor. Instead of using the biological reactor, another flask was made with only the salt solution. A comparison was made between the new flask (with bacteria) and this flask (without bacteria). The inlet and

outlet gases of both were analyzed with the Kitagawa detection tubes. The inlet gases of both had a concentration of 10 ppm. The outlet gases for the new flask had no staining on the tube resulting in no H₂S presence while the outlet gases for the flask without bacteria had a concentration of 1 to 2 ppm of H₂S present.

CONCLUSIONS

The amount of time needed to do this thesis project was underestimated. The time assumed for the T. thiooxidans to grow was longer than expected. Approximately, two to three months instead of a couple of weeks was needed to insure that the T. thiooxidans was growing in chains and colonies. This thesis project was not fully completed. The bugs did not have enough time to grow, so they were not injected into the aerobic biological reactor. No conclusion can be made on the efficiency of this reactor to degrade or eliminate odorous gases such as hydrogen sulfides. The Kitagawa Precision tubes proved to be a good and easy method for analyzing the concentration of H₂S gas (inlet or exit).

RECOMMENDATIONS

This project can be continued using spun glass wool as the packing material to determine the feasibility of using this type of reactor to degrade or even eliminate odorous gas such as hydrogen sulfides. Other noncondensibles gases such as sulfur oxides or nitrogen oxides can be used instead of hydrogen sulfides. Also, other types of packing materials can be used such as wood chips, plastic straws, or even compost.

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Figure I

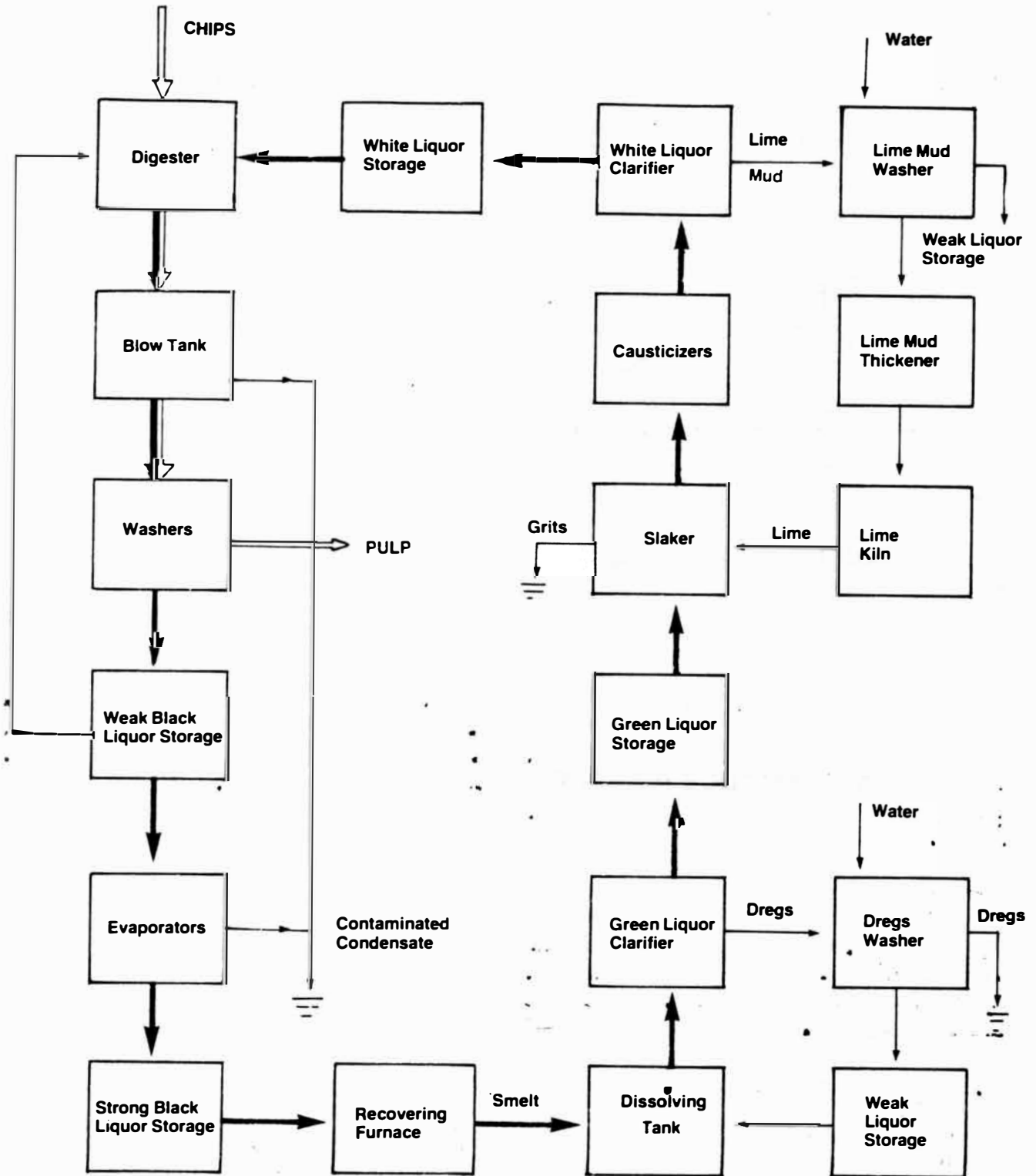


FIGURE 7-3. Kraft process.

Figure II

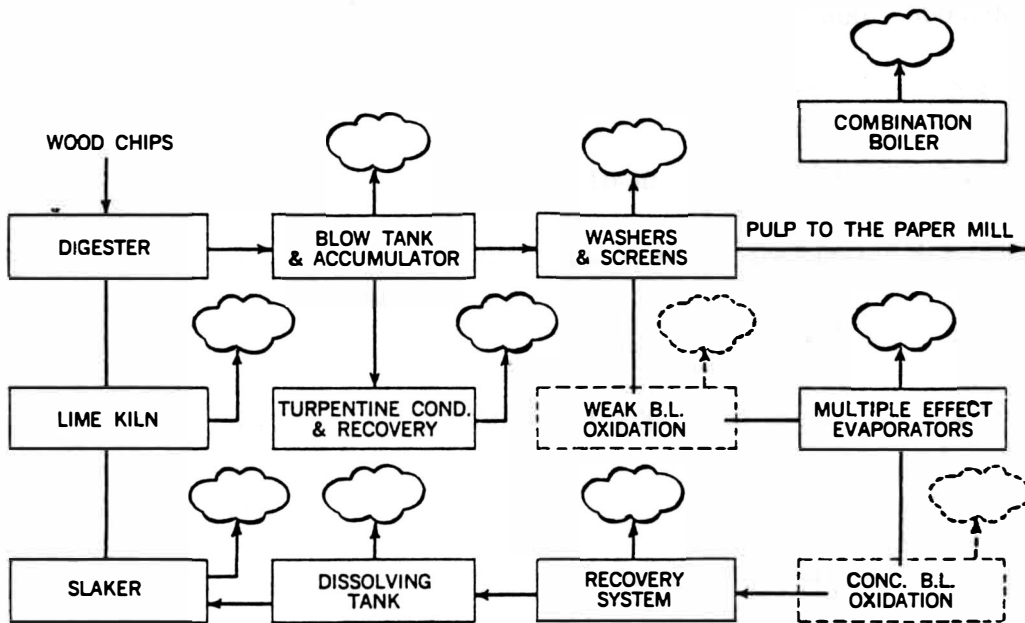


FIGURE 27-2. Potential air emission sources in a kraft pulp mill.

Table I

TABLE 1-3
TYPICAL REDUCED SULFUR GAS CONCENTRATIONS FROM KRAFT
PULP MILL SOURCES

<u>Emission Source</u>	<u>Concentration (ppm by volume)</u>			
	<u>H₂S</u>	<u>CH₃SH</u>	<u>CH₃SCH₃</u>	<u>CH₃SSCH₃</u>
Digester, Batch:				
Blow Gases	0-1,000	0-10,000	100-45,000	10-10,000
Relief Gases	0-2,000	10-5,000	100-60,000	100-60,000
Digester, Continuous	10-300	500-10,000	1,500-7,500	500-3,000
Washer Hood Vent	0-5	0-5	0-15	0-3
Washer Seal Tank	0-2	10-50	10-700	1-150
Evaporator Hotwell	600-9,000	300-3,000	500-5,000	500-6,000
BLO Tower Exhaust	0-10	0-25	10-500	2-95
Recovery Furnace (after direct contact evaporator)	0-1,500	0-200	0-100	2-95
Smelt Dissolving Tank	0-75	0-2	0-4	0-3
Lime Kiln Exhaust	0-250	0-100	0-50	0-20
Lime Slaker Vent	0-20	0-1	0-1	0-1

Both oxides of sulfur (SO_x) and oxides of nitrogen (NO_x) can be emitted in varying quantities from specific sources in the kraft chemical recovery system. The major source of sulfur dioxide (SO₂) emissions is the kraft chemical recovery furnace, because of combustion of sulfur-containing black liquor fuel. Under certain conditions, somewhat similar quantities of sulfur trioxide (SO₃) can be released to the atmosphere, particularly when residual fuel oil is added as an auxiliary fuel (9). Lesser quantities of SO₂ can also be released from the lime kiln and smelt dissolving tank. Trace quantities of sulfur oxides may also be released from other kraft mill sources. Oxides of nitrogen can be formed in any fuel combustion process by the reaction between oxygen and nitrogen at elevated temperatures.

Table II

TABLE 1-4
 TYPICAL REDUCED SULFUR GAS EMISSION RATES FROM KRAFT PULP
 MILL SOURCES

<u>Emission Source</u>	<u>Emission Rate, kg sulfur per metric ton of air dried pulp</u>			
	<u>H₂S</u>	<u>CH₃SH</u>	<u>CH₃SCH₃</u>	<u>CH₃SSCH₃</u>
Digester, Batch:				
Blow Gases	0-0.1	0-1.0	0-2.5	0-1.0
Relief Gases	0-0.05	0-0.3	0.05-0.8	0.05-1.0
Digester, Continuous	0-0.1	0.5-1.0	0.05-0.5	0.05-0.4
Washer Hood Vent	0-0.1	0.05-1.0	0.05-0.5	0.05-0.4
Washer Seal Tank	0-0.01	0-0.01	0-0.05	0-0.03
Evaporator Hotwell	0.05-1.5	0.05-0.8	0.05-1.0	0.05-1.0
BLO Tower Exhaust	0-0.01	0-0.1	0-0.4	0-0.3
Recovery Furnace (after direct contact evaporator)	0-25	0-2	0-1	0-0.3
Smelt Dissolving Tank	0-1	0-0.8	0-0.5	0-0.3
Lime Kiln Exhaust	0-0.5	0-0.2	0-0.1	0-0.05
Lime Slaker Vent	0-0.01	0-0.01	0-0.01	0-0.01

The major constituent formed in nitric oxide (NO), a small portion of which can be oxidized to form nitrogen dioxide (NO₂): together they are classified as total oxides of nitrogen. Nitrogen oxide emissions from kraft pulp mill process sources, such as the recovery furnace and lime kiln, are normally lower than for most other fuel combustion processes. This is primarily due to the large quantities of water present in black liquor and lime and which act as a heat sink to suppress the flame temperature. Larger quantities of oxides of nitrogen can be formed, however, when auxiliary fuels such as natural gas or fuel oil are added to the recovery furnace.

TABLE 27-2. Characteristics of kraft mill reduced sulfur gases.

<i>Compound</i>	<i>Chemical Formula</i>	<i>Type of Odor</i>	<i>Aprox. Odor Threshold</i>
hydrogen sulfide	H ₂ S	rotten eggs	1 ppb
methyl mercaptan	CH ₃ SH	rotten cabbage	1 ppb
dimethyl sulfide	CH ₃ SCH ₃	vegetable sulfide	10 ppb
dimethyl disulfide	CH ₃ SSCH ₃	vegetable sulfide	10 ppb

Table III

Table IV

Table 4. Effects of Hydrogen Sulfide Inhalation on Humans^a

Number of people exposed	Concentration, mg/m ³	Duration of exposure	Effect
1	17,000		death
1	2,800–5,600	<20 min	death
10	1,400	<1 min	unconsciousness, abnormal ECG; death of one person
342	1,400–2,800	<20 min	hospitalization of 320, death of 22 including 13 in the hospital, residual nervous system damage in 4
5	1,400	instant	unconsciousness, death
1	1,400	<25 min	unconsciousness, low blood pressure, pulmonary edema, convulsions, hematuria
4	400–760		unconsciousness
1	320	20 min	unconsciousness, arm cramps, low blood pressure
78	20–35		burning eyes in 25, headache in 32, loss of appetite in 31, weight loss in 20, dizziness in more than 19
6,500 population of Terre Haute, Indiana	15–20 0.003–11	4–7 h intermittent air pollution episodes over a 2-mo period	conjunctivitis nausea in 13, headache, shortness of breath in 4, sleep disturbance in 5, throat and eye irritation in 5

^a Ref. 99.

Table V

TABLE 1. Characteristics of the Filter Bed and Operating Conditions

height of the packing	1.2 m
temperature	25–30°C
VOCs concentrations in waste gases (g/m ³)	
Toluene	0.75–3.76
Ethanol	1.89
pressure drop	< 6 cm H ₂ O/m
superficial air velocity	70.70 m ³ /m ² .h
humidity of air at the inlet of biofilter	93%
mean residence time of the gas phase	51 sec

Figure III

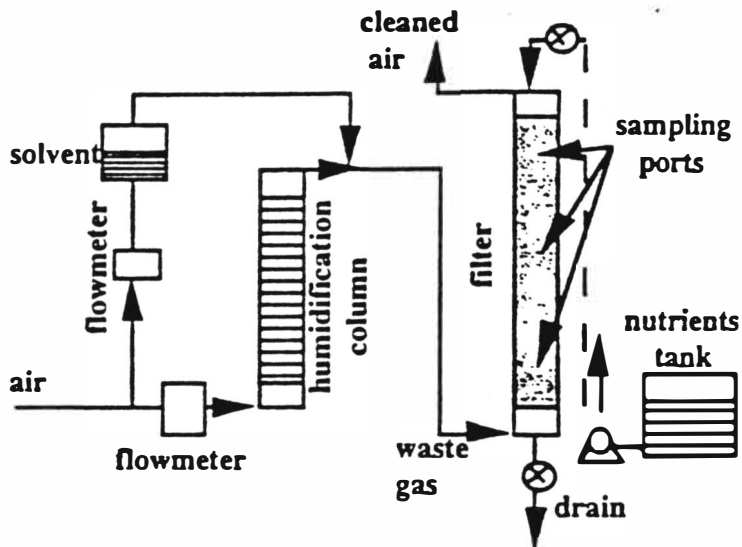


Table VI

Test Results with Methylene Blue Method

mL of H ₂ S	Concen. within bag	Volume of gas injected	Absorbance
10	50 ppm	6 mL	0.79%
10	50 ppm	12 mL	hardly noticeable
10	50 ppm	18 mL	1.30%

Table VII

Test Results with Kitagawa Precision Gas Detectors

mL of H ₂ S	Test #1	Test #2
10 mL	25 ppm	6 ppm

Figure V

