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16. Abstract Alternatives to control wastewater odors on board Washington State ferries and during discharge of the wastewater to sewerage systems were formulated, evaluated and tested. Holding tank aeration, using compressed air injection to a recycle line is an effective method. Sulfide is microbially oxidized, and anaerobic sulfate reducing bacteria are suppressed. Engineering and lab studies and a simulation model of the process were used to estimate suitable design parameters and costs. A prototype installation is recommended for optimization of operation. The addition of slug dosages of H_2O_2 was also found to be effective in laboratory and on-board vessels. The twice daily dose of about 50 mg/l should be stirred into the holding tank using recycle mixing. Peroxide was found to oxidize sulfide, increase dissolved oxygen and suppress sulfate reducing bacteria. Bottom suction sludge hoppers must be installed to prevent accumulation of sludge in tank bottoms. Other alternatives, including chlorine addition, pH increase, iron sulfide precipitation and toxic odor control compounds, were found ineffective and/or uneconomic. Other finds are that sulfide is produced primarily from reduction of sulfates from the saltwater flushing water. Production is primarily in the slime layer on the bottom and sides of the holding tanks. On-shore force mains are sites of sulfide production during stagnant periods between tank pumpouts. These force mains should be flushed with clean salt water once each day. The discharge from ferry holding tanks was evaluated for hydraulic, organic loading, and salt toxicity effects on existing and planned sewage plants. No significant impacts were found.					
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FINAL REPORT

A STUDY OF WASTEWATER HANDLING, HOLDING AND DISPOSAL
FROM WASHINGTON STATE FERRIES

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and in cooperation with

U. S. Department of Transportation
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I. Summary and Conclusions

The Washington State Ferry fleet includes 18 vessels operating on eight major routes between 20 terminals. The vessels are equipped with wastewater holding tanks for collection and holding of salt water urinal and toilet waste as well as all fresh water waste from galleys, sinks, showers and drinking fountains. These systems are intended to hold wastes for one day or more prior to pumping to municipal sewerage systems for treatment and disposal. Odor problems on board some of the vessels, in the vicinity of some terminals and along sewers have been associated with the ferry waste water discharge and militate for odor control measures. Several alternative odor control methods for a marine holding tank system, including chemical additions, aeration, conversion to fresh water and increased pumpout frequencies, have been evaluated in this study. Waste aeration and hydrogen peroxide addition were found to be the most effective.

Holding tank aeration, using air injection to a recycle line, has been shown to be an effective method of odor control. A new recycle line would be installed to recirculate the contents of the sewage holding tank, and air would be injected into this stream using a new compressor.

Oxygen in the injected air allows sulfide in the wastewater to be oxidized chemically or microbiologically to sulfate. In the presence of oxygen, anaerobic sulfate reducing bacteria will be suppressed, and sulfide generation will be stopped. If 1 mg/l dissolved oxygen is maintained in the wastewater little or no sulfide build-up is expected, and odor problems should be eliminated. The results of a mathematical simulation of the recycle system indicated that a system of air injection at the rate of 10 scfm to a 400 gpm recycle flow rate (maintained at 30 psi) for ten minutes per hour will be sufficient to maintain dissolved oxygen and prevent sulfide production.

Retention time at high pressure should be maximized by controlling the pressure with a valve located near the downstream end of the return line. Use of a pressurized retention tank might also be desirable and could be evaluated in pilot studies. Procedures for a pilot study to confirm these simulation results are discussed.

Thorough tank cleaning is especially important for this alternative. A dense, oxygen demanding microbial population could develop unless the sewage pump suction is relocated to the tank bottom to improve the removal of solids.

Cost estimate for the system based on a ten minute per hour aeration time results in a total annual cost of about \$2,120 including amortized installation costs and operation (Table 1). Detailed costs are estimated for the Evergreen State Class vessels. The costs cannot be directly extrapolated to the entire fleet, but the relative differences between alternatives should be consistent.

Hydrogen peroxide addition was also found to be an effective odor control alternative. Bottle tests showed inhibition of sulfide generation for two days with doses of 40 to 60 mg/l. In on-board tests, doses of 40 to 65 mg/l inhibited sulfide production for 3 to 7 hours after oxidizing high concentrations of sulfide. It was concluded that once the tanks were conditioned by high doses to remove residual sulfide, longer periods of inhibition would be achieved by lower doses.

With respect to the chemical handling, feeding and mixing system proposed by Parrish, Ferguson and Sylvester (1976), it was concluded that slug addition be provided rather than continuous injection to take advantage of the inhibiting capabilities of hydrogen peroxide.

Table 1. Cost Summary of Recommended Odor Control Procedures for the
M.V. Evergreen State

Recycle Aeration

Capital	\$12,240
Amortized Capital	1,224
Annual Operation and Maintenance	<u>896</u>
<u>Annual Cost</u>	\$ 2,120

Peroxide - Manual Batch Addition - Recycle Mixing

Capital*	\$ 5,110
Amortized Capital	511
Annual Operation and Maintenance	<u>686</u>
<u>Annual Cost</u>	\$ 1,197

* Capital costs for this alternative include a direct recycle connection and bottom suction. These system changes were determined during report preparation, and the cost estimates are not as detailed as others presented in the report.

The results of on-board tests indicate that recycle mixing during chemical addition is necessary. From a cost standpoint, manual addition of hydrogen peroxide slug doses with minimal mixing and improved tank cleaning may be the best alternative. Based on the recommended dose of 900 grams added each day in two doses, the annual cost will be about \$1,200 compared with \$2,120 for the aeration system. This use of hydrogen peroxide will require shorter vessel layup for installation of bottom suction and line changes. No maintenance of the system should be needed. The addition of the doses will require care since the peroxide must be handled directly by crew members. The method is easily adaptable to all vessels in the ferry fleet. Conclusions from monitoring during a trial period are included in the report.

There are non-economic differences between peroxide and aeration that tend to favor the aeration alternative. Hydrogen peroxide addition requires special handling procedures on-board and may cause logistic problems in supplying the chemical to the vessels. Use of 8% H_2O_2 solution requires that relatively large quantities (more than 2 gallons) be added each day.

Aeration, on the other hand, is an automated system and will eliminate crew contact; still, periodic maintenance of system components will be required. As opposed to the hydrogen peroxide alternative, the air injection system will result in the discharge of fresh, aerobic sewage with a reduced BOD and will reduce the possibility of further sulfide production in shore sewage facilities. By maintaining aerobic conditions, the aeration system may also be more effective in preventing odors during problem situations, such as when complete pumping of the tank is not possible. The limited mixing and turbulence within the tank provided by the recycle of waste may tend to prevent the accumulation of solids. It is noted, however, that continued accumulation

of solids will result in excessive oxygen demand and anaerobic conditions may still develop. Good tank cleaning is required.

Overall, aeration is more effective, more reliable, easier and safer to operate. These factors are more important than the economic difference with manual slug addition of peroxide, which is the least cost alternative.

The aeration system proposed is more expensive than the manual addition of peroxide but is significantly less expensive than the other alternatives that were proposed for preliminary design and evaluation. In addition and compellingly, none of the other methods were demonstrated to be technically feasible. All had significant drawbacks or unanswered technical questions.

Chlorine was effective in inhibiting sulfide production in bottle tests with a dose of 40 mg/l (80% of the chlorine demand), but a dosage of 80 mg/l (100% of the chlorine demand) was much less effective when applied to the holding tank. This reduction in efficiency was attributed to the concentration of the sulfide producing bacteria in wall slimes, to sludge deposits which consumed chlorine, and to the poor initial mixing in the tank. The oxidation of sulfide by chlorine was also found to be inefficient, requiring a ratio of 4.4 to 10.8 parts chlorine per part sulfide oxidized for bottle tests and ratios of 16 to 26.5 required for on-board slug doses.

Alteration of pH was also found to be ineffective. The elevation of pH to a level necessary for disinfection (12.5) was found to require exceedingly high doses of base. Heavy precipitation of calcium and magnesium solids was found to occur at pH values over 10. Relatively small doses of base were required to achieve pH 9 with no significant solids production. Although the on-board odor problem might be eliminated at this pH, it is likely that sulfide production would continue at this pH level and cause potential on-shore problems when the pH is lowered as it mixes in the shore sewage systems.

A commercial odor control agent extensively used prior to and during the study, E-Clor, was found to be ineffective in reducing sulfide generation in bottle tests at doses below 40 mg/l, and was ineffective in oxidizing sulfide. The on-board effectiveness of E-Clor is also doubtful since high concentrations of sulfide were measured in discharge from the M.V. Elwha and in the holding tanks of the M.V. Tillikum and M.V. Klahowya. All these vessels were using E-Clor at the time. Other factors, including potential health hazards, possible detrimental effects on treatment processes, and persistent toxicity to aquatic organisms led to the conclusion that the use of this agent is unacceptable and should be discontinued.

Waste Characteristics and Generation

Characteristics of the waste from the ferry vessels were found to be highly variable but generally similar to normal domestic sewage with the constituents of seawater superimposed. Based on the average salinity of seawater in Puget Sound, the waste was found to be about 90% seawater, a consequence of the seawater flushing system aboard the vessels. The conditions of pH, temperature, nutrient supply and dissolved oxygen were found to be in a highly favorable range for the bacterial production of sulfide, which was used as an indicator of odor intensity.

The waste was found to accumulate at about 1.8 gallons per passenger during the summer study period for the study route (Fauntleroy-Vashon-Southworth). Other longer routes in the system have a higher rate of waste accumulation per passenger.

It was concluded that the primary site of sulfide production was within wall slimes and sludge deposits. In the 10,000 gallon tank aboard the M.V. Tillikum, the rate of sulfide production averaged 14 grams per hour, although this rate was highly variable. The production per unit area average $0.40 \text{ grams/m}^2 \cdot \text{hr.}$

Effects at Terminals and in Receiving Sewage Systems

Three main effects were assessed, including sulfide generated in force mains which are stagnant between pumpouts, effects of the high salinity wastewater on biological treatment processes and hydraulic impacts of high pumpout rates. There were several findings from this portion of the study.

No problems due to the salinity or to any other characteristics of the ferry waste are expected at any treatment plants that will receive the waste.

Sulfide generation in force mains probably occurs near the Fauntleroy and Edmonds terminals during periods of stagnation between pumpouts. Force main flushing should be implemented. Pumpout schedules should be staggered throughout the day, with thorough flushing once each day before the longest stagnation period.

Specific considerations at the terminal sites included: Design of the sewer system at the Anacortes terminal should be coordinated closely with the consulting engineer for the city, in order to properly size the lift station and to avoid stagnation and the resultant sulfide generation in the force main.

The discharge of ferry wastewater at Mukilteo could impose hydraulic overloads on the present treatment plant.

The only other hydraulic problem is at the Seattle terminal where a section of the gravity sewer has limited flow capacity. Simultaneous discharge from two ferries would exceed the capacity and should be avoided.

II. Background

The Federal Water Quality Control Act of 1965 required that states establish water quality standards for the enhancement of coastal waters and establish programs for achieving these standards. The State of Washington does not allow the discharge of any organic or inorganic matter that shall cause or tend to cause pollution of the waters of the state (RCW90.48). The State Water Pollution Control Commission established water quality standards in 1967 and classified most of Puget Sound and the Strait of Juan de Fuca, except for some port areas, as Class AA Extraordinary. Implementation of these water quality standards has not been applied to discharges of wastewater from watercraft. The Federal Water Quality Improvement Act (PL91-224) authorized the U.S. Coast Guard to promulgate standards for marine sanitation devices to prevent the discharge of untreated or inadequately treated wastewater into the navigable waters of the United States.

In recognition of the fact that these regulations would eventually prohibit the overboard discharge of untreated wastewater, the Washington State Ferries in 1970 authorized a study to evaluate the feasible alternatives for acceptable disposal of shipboard sewage (Tudor Engineering Co., 1970). This study recommended the installation of sewage holding tanks on all vessels and on-shore disposal of wastewater. At the present time, sewage holding tanks have been installed on all vessels, and on-shore sewage transfer facilities have been built, or are being planned, on all routes.

The eighteen vessels in the fleet operate over seven main routes and have an average of more than 40,000 passenger trips each day. The characteristics of the vessels and their wastewater holding systems are tabulated in Table 2, with the ferry routes and passenger volumes shown in a schematic diagram (Figure 1).

The increasing public concern for the protection of the environment and the desire for clean waterways has been shown by the adoption of PL92-500 in

Table 2: Washington State Ferries Fleet - Summer 19/6

Vessel Name	Length	Capacity Autos Passengers	Wastewater Holding Tanks Number Total Capacity	Route
M.V. Spokane	440 ft.	206 2000	2 20,000 gal.	Seattle - Winslow
M.V. Walla Walla	440 ft.	206 2000	2 20,000 gal.	Seattle - Winslow
M.V. Hyak	382 ft.	160 2500	2 10,000 gal.	Seattle - Bremerton
M.V. Yakima	382 ft.	160 2500	2 10,000 gal.	Seattle - Bremerton
M.V. Elwha	382 ft.	160 2500	2 10,000 gal.	Edmonds
M.V. Kaleetan	382 ft.	160 2500	2 10,000 gal.	Anacortes
M.V. Evergreen State	310 ft.	100 1000	1 10,000 gal.	Anacortes
M.V. Klahowya	310 ft.	100 1140	1 10,000 gal.	Fauntleroy
M.V. Tillikum	310 ft.	100 1140	1 11,000 gal.	Fauntleroy
M.V. Quinault	256 ft.	75 665	1 5,000 gal.	Fauntleroy
M.V. Illahee	256 ft.	75 800	1 5,000 gal.	Edmonds
M.V. Nisqually	256 ft.	75 665	1 5,000 gal.	Anacortes
M.V. Klickitat	256 ft.	75 800	1 5,000 gal.	Anacortes
M.V. Olympic	207 ft.	55 605	1 2,500 gal.	Port Townsend
M.V. Rhododendron	226 ft.	65 546	1 2,500 gal.	Mukilteo
M.V. Kulshan	242 ft.	65 350	1 1,800 gal.	Mukilteo
M.V. Hiyu	150 ft.	40 200	1 1,000 gal.	Tacoma

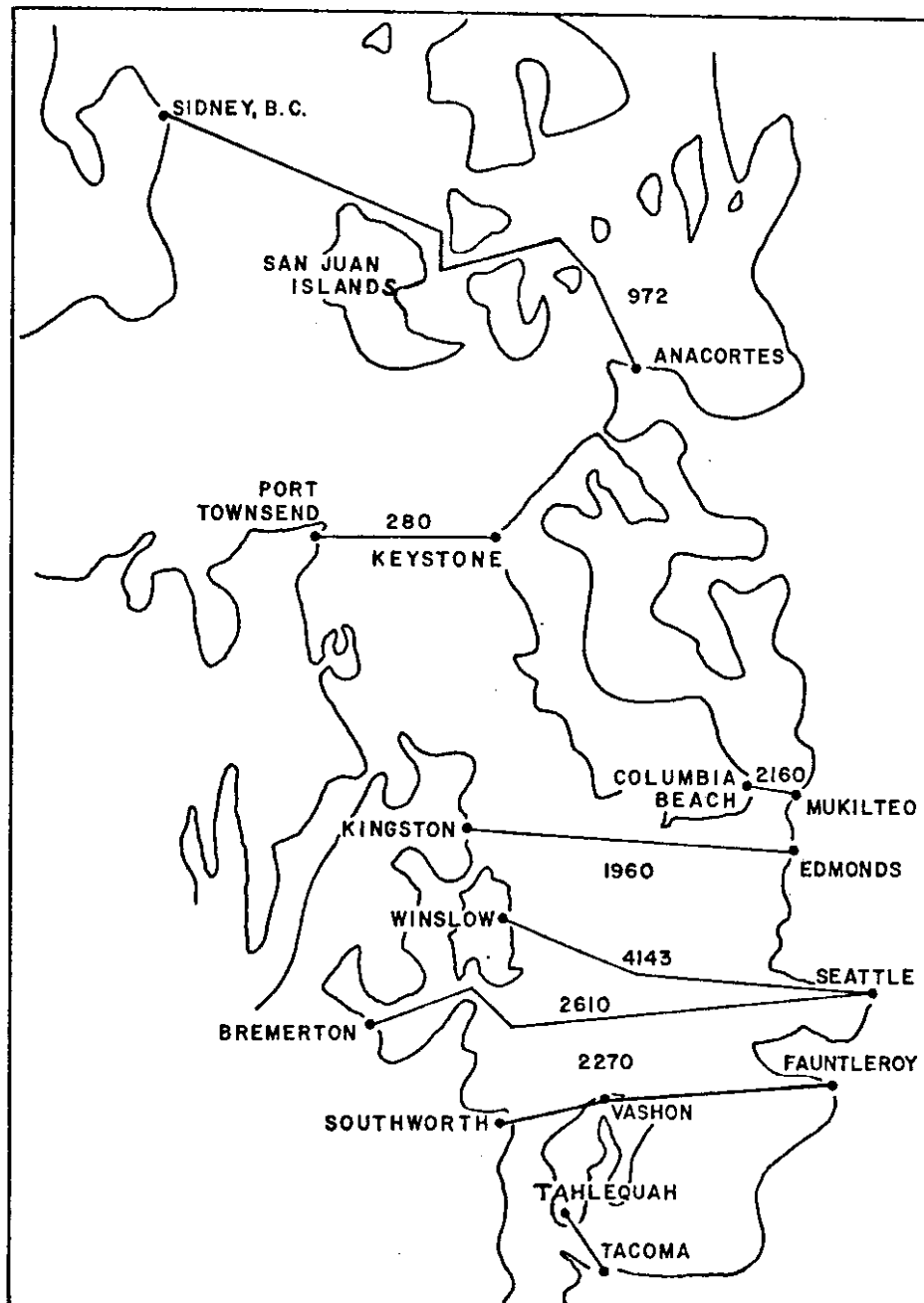


Figure 1. Washington State Ferry Routes and 1976 Passenger plus Vehicle Driver Volume (in thousands).

1972. The requirements of the law are reflected in standards that the Coast Guard and Environmental Protection Agency have developed for Marine Sanitation Devices (Federal Register, 1975 and 1976). The ferry system has set an excellent example by implementing on-shore disposal prior to these regulations.

The sewage holding tank systems are designed with a capacity for at least 24 hours service, when feasible, so the tank(s) can be pumped ashore during the night time layup or at some convenient time each day (Nickum, 1970). The holding tank systems range in size from 5,400 gallons to 20,000 gallons. They consist of one or two tanks of about 5,000 or 10,000 gallon capacity and of variable shape depending on the space available on the different classes of vessels. The holding tanks receive both salt water sanitary wastewater from toilets and urinals and fresh water wastewater from sinks, showers and galley. On-board pumps with a rated capacity of 200-500 gpm are used to pump the wastewater from the holding tanks for on-shore disposal. Wash nozzles have been installed to permit routine washing of the holding tanks.

Odor problems developed shortly after the first systems were installed. These odors present both technical and aesthetic problems. Odors produced on-board the ferries have been reported to be very strong, even overpowering, and are probably caused mainly by bacterial reduction of sulfate in the wastewater to form hydrogen sulfide. Various chemicals have been added to the wastewater to try to control these odors but have not been effective and are fairly expensive. Improved design of the holding tanks, use of exhaust blowers, and venting the sewage tanks to the exhaust stacks have each been applied on some vessels and have been successful in reducing odor problems on the vessels.

Objectionable odors have also occurred at the loading docks and in nearby sewers when wastewater is pumped ashore. Besides creating a disagreeable odor, the hydrogen sulfide evolved from these wastes may cause corrosion of concrete sewers and pose a hazard to sewer workers. If bacterial action in the sewer system reduces sulfates in the wastewater as it flows through the sewer, additional hydrogen sulfide may be generated and cause odor and corrosion problems.

Study Organization:

In March 1976, the Washington State Highway Commission authorized a research contract to study wastewater handling, holding and disposal from ferries. The project was carried out in four parts. In the first phase, alternatives for control of on board odors were formulated and evaluated. For selected methods, conceptual plans were prepared for sizing and description of equipment to be used. Chemical dosages and recommended operating procedures were determined, and estimates of installation, chemical and operating costs were made for budget comparison (Parrish, Ferguson and Sylvester, 1976).

In the second phase, laboratory and field tests were conducted to ascertain the typical wastewater composition, the potential for odor production and the effectiveness of the various control alternatives. These studies (Browne, Ferguson and Sylvester, 1976) resulted in refinement of the conceptual design, operating procedures and costs developed in the first phase.

In the third phase of the study, possible effects of the waste discharge on on-shore facilities were described and assessed. In the instances where significant impacts were found, procedures were recommended for mitigating the impacts (Lellelid, 1977).

Finally, monitoring the use of hydrogen peroxide (H_2O_2) added in twice daily slug dosages was carried out to evaluate its effectiveness and the possible need for improved tank cleaning and tank mixing. Force main flushing was also evaluated.

This report includes the significant findings of the study that relate to the recommended alternatives and a summary of all project activities. The report is organized into three principal sections. In the first, the relation of odor to hydrogen sulfide production is discussed and measurements of hydrogen sulfide production and the wastewater characteristics are described. In the second, the alternatives for on-board odor control are presented with the pertinent experimental results and engineering evaluation. In the third section, the possible on-shore impacts are evaluated.

It was necessary to limit the scope of the study to certain vessels and certain runs in order to gather detailed information for careful comparisons. The M. V. Tillikum and M. V. Klahowya, in use on the Fauntleroy-Vashon-Southworth run, were chosen as study vessels due to their close proximity to the University of Washington and to the accessibility of the holding tanks for sampling. Likewise, the design and cost estimates were made for vessels of the Evergreen State class which includes the M. V. Evergreen State, M. V. Klahowya and M. V. Tillikum. All alternatives were developed so that the same methods would be used on all fleet vessels and so that vessels could be used interchangeably on all runs. Thus while the experimental data and design cost estimates cannot be directly extrapolated and applied to the whole fleet, the relative differences between options can be generalized to all vessels and all runs.

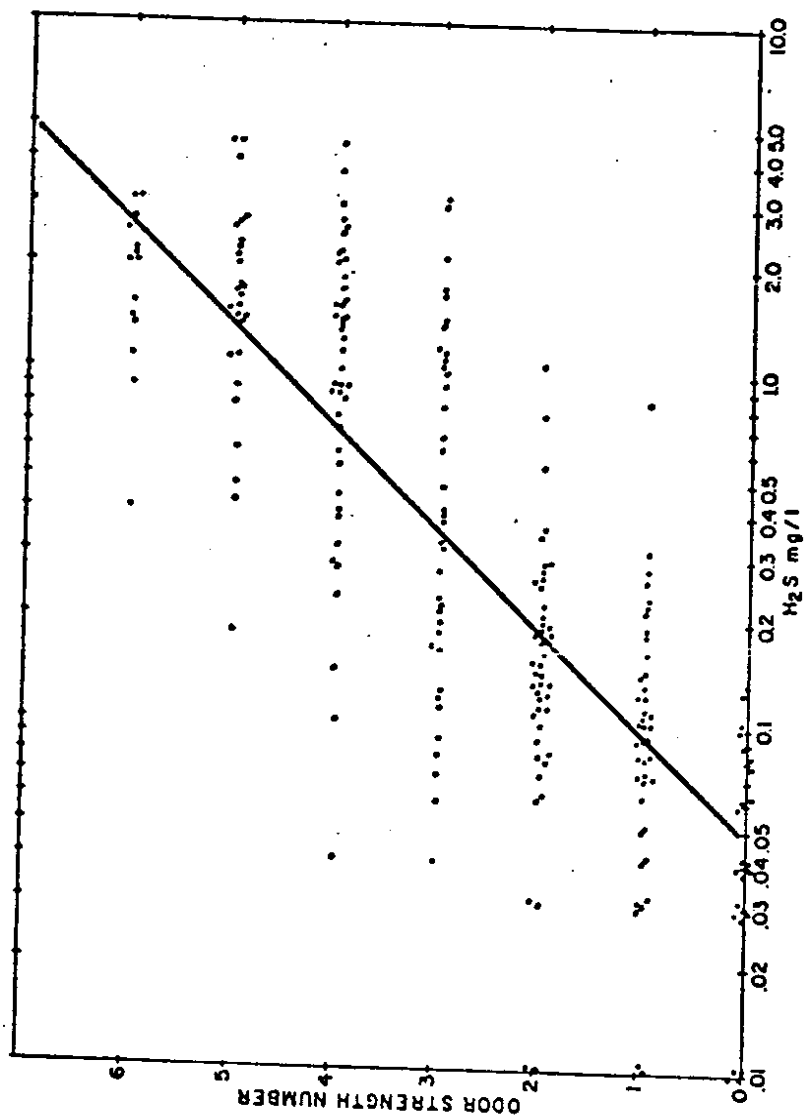
III. Odor Production in Wastewater - Role of Hydrogen Sulfide

The control of sewage odor has been extensively studied in the past. While much of the information concerns odor problems and control methods for flowing, freshwater sewage (a different situation than in marine wastewater holding tanks), pertinent portions of the previous studies are a useful background for this study.

Odor and Hydrogen Sulfide

Odor causing substances in wastewater may be classified as either inorganic or organic gases. Although many inorganic gases are formed by bacterial activity in sewage, only ammonia (NH_3) and hydrogen sulfide (H_2S) are of an odorous nature (Dague, 1972). Over 50 different organic gases have been identified in sewer air, principally including mercaptans, paraffinic amines, aldehydes and organic acids. The concentrations of most of these gases have been correlated directly with the level of hydrogen sulfide present (Thistlethwayte, 1972). One such correlation from Cole et al.(1976) is shown in Figure 2. The conditions which lead to the production of hydrogen sulfide **have** been found also to encourage the reduction of organic materials to odor producing compounds (Dague, 1972). These relationships have led to the traditional use of hydrogen sulfide as a measure of odor. By controlling the production of sulfides, it is assumed that other odor sources will also be controlled.

Hydrogen sulfide (H_2S) is a gas with a strong odor characteristic of rotten eggs. A concentration of 300 ppm (volume) in the air is toxic (EPA, 1974). The odor threshold for detecting H_2S is 10^{-4} ppm (v) and concentrations above 1 ppm (v) are usually objectionable (Summer, 1963 and Thistlethwayte, 1972). The amount of H_2S in the air is proportional to the H_2S dissolved in the wastewater. The concentration of hydrogen sulfide in the air is usually



Strength (quantity)

0 No odor

1 Faint

2 Noticeable

3 Definite

4 Strong

5 Overwhelmingly strong

6

7

8

9

10

Figure 2. Correlation of odor and hydrogen sulfide concentrations from Cole (1976).

2 to 20% of the amount predicted to be in chemical equilibrium with the amount dissolved in the water (EPA, 1974). As shown in Figure 2, concentrations of less than 0.2 mg/l H_2S in wastewater generally cause only faint odor problems. This value can be selected as a criteria for evaluating sulfide control processes.

The Henry law constant may be expressed as follows:

$$[H_2S] = K_H P_{H_2S}$$

where P_{H_2S} is the partial pressure of hydrogen sulfide in atmospheres and $[H_2S]$ is the molar activity of H_2S in solution. Various units are used for measuring hydrogen sulfide in solution and in the gas phase. Equivalences in solution are 10^{-3} Moles/liter = 34 mg/l measured as H_2S = 32 mg/l as S. In the gas phase, 10^{-6} atmospheres = 1 ppm (v) = 1.2 ppm (wt) as H_2S . K_H at 20°C has a value of 0.10.

Hydrogen sulfide is a weak diprotic acid with acid dissociation constants of 10^{-7} and approximately 10^{-13} . The fraction of sulfide present as H_2S depends on the pH of the solution; virtually all the sulfides are in this form below pH 6. The fraction decreases by about a factor of 10 for every unit increase in pH above 7 as shown in Figure 3.

Sulfide Generation

Sulfides, and their associated odor problems, are produced in sewage by the bacterial reduction of various sulfur containing constituents; of most importance is inorganic sulfate but organic sulfur, especially proteins with thioamino acids, may also be a significant source (Thistlethwayte, 1972). In aerobic sewage, bacteria use dissolved oxygen as an electron acceptor for the oxidation of organic substrates. When the waste is devoid of oxygen, a

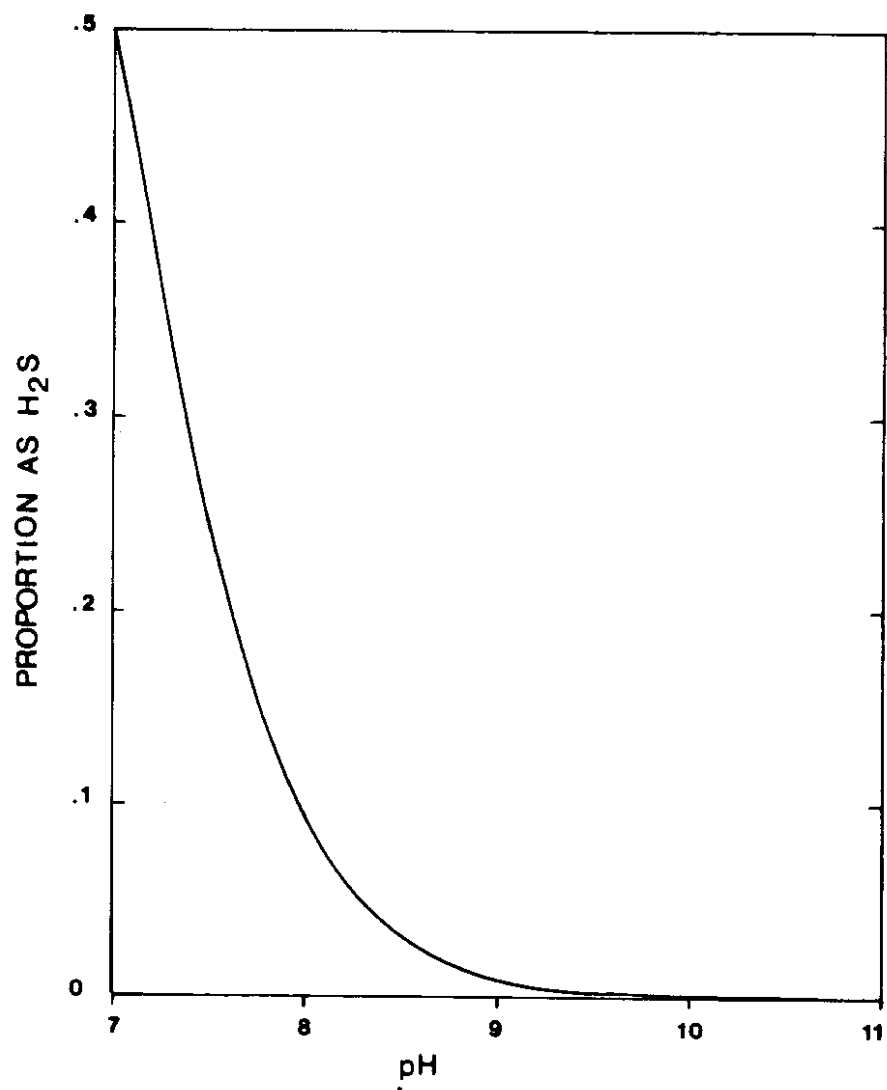


Figure 3. Proportion of total sulfide in wastewater present as hydrogen sulfide for pH values above 7.

specialized group of obligate anaerobic bacteria (most notably Desulfovibrio desulfuricans) is able to use sulfate ion for the same purpose by reducing sulfate to sulfide.

Pomeroy and Bowlus (1946), in an extensive survey and study, investigated the effects of several parameters on sulfide production. They found that sulfate reducing bacteria are able to proliferate throughout a wide range of pH values (6-9) with an optimum of between pH 7.5 and 8.0. Sulfide generation was found to be independent of sulfate concentration with initial sulfate concentrations over 100 mg/l (33 mg/l as S). Baumgartner (1934) found the optimum temperature for production of sulfide to be between 30 and 37°C. Significant inhibition of sulfide generation was found at 7°C.

The oxidation-reduction potential (ORP) is a general measure of the relative concentrations in the water of oxidants (oxygen, nitrate) and reductants (sulfide, ammonia). Sulfate reducing bacteria require a low ORP of between -300 and -200 millivolts. Although the concept of ORP is useful in generally describing the condition of biotic systems, the definition is based on equilibrium conditions. Since biological systems are not in a state of thermodynamic equilibrium, the ORP cannot be directly measured. The potential between an inert electrode and a reference electrode is often used as a related parameter.

Marine wastewaters with high sulfate concentrations, moderate temperatures and pH values, and high organic concentrations provide a very suitable media for the growth of sulfate reducers and for the production of hydrogen sulfide. The holding tanks, which typically have very little mixing, a relatively large wetted surface area and incomplete cleaning between cycles of use are a nearly ideal vessel for sulfide production.

It was noted that sewage samples placed in bottles exhibited a lag period, which did not occur in sewers, before sulfide generation began (Baumgartner,

1934). Pomeroy and Bowlus (1946) concluded that the generation of sulfide primarily occurred in slimes along the sides and in sludge layers in sewers and not within the flowing body of sewage. Counts of sulfate reducing bacteria in sewage and sewage solids by Heukelekian (1948) confirmed this concept. The seeding with organisms and maintenance of a large slime-covered surface area in the holding tanks are important factors in sulfide production.

IV. Waste Characterization and Sulfide Production

It was fundamental to subsequent studies of odor control and of effects on on-shore facilities to determine the characteristics of the wastewater and to investigate the rate and mode of sulfide formation. These studies were conducted on the M. V. Klahowya and M. V. Tillikum during summer, 1976 when both vessels were in service on the Fauntleroy - Vashon - Southworth run. All wastewater samples used in the above studies were taken directly from the on-board holding tanks on the two study vessels.

Vessel Tank Configurations

Both the M. V. Tillikum and M. V. Klahowya have 10,000 gallon holding tanks suspended over the No. 1 end shaft alley. Figure 4 shows the general dimensions of the tanks. The tank on the M. V. Klahowya has a flat bottom with the sewage pump suction located at one end approximately 6 inches above the bottom. A 1/2 inch sample tap was installed by Washington State Ferries' personnel next to the pump suction pipe at the same height above the bottom. A bolted access hatch is located on the top of the tank in one corner. A 1-1/2 inch drain valve is located in the center of the tank on the bottom.

The tank on the M. V. Tillikum is of similar construction except the bottom is sloped to the lengthwise center of the tank (1 ft: 6-1/2 ft). The pump suction nozzle is located on the bottom of the tank on this center line. A 1-1/4 inch sample valve was installed by Washington State Ferries at one end of the tank 6 inches above the bottom. The access hatch on the Tillikum tank is located near the middle of the tank along one edge.

Waste Characterization and Sulfide Production

Samples were taken from the M. V. Tillikum and M. V. Klahowya to verify the wastewater composition and to investigate the production of hydrogen sul-

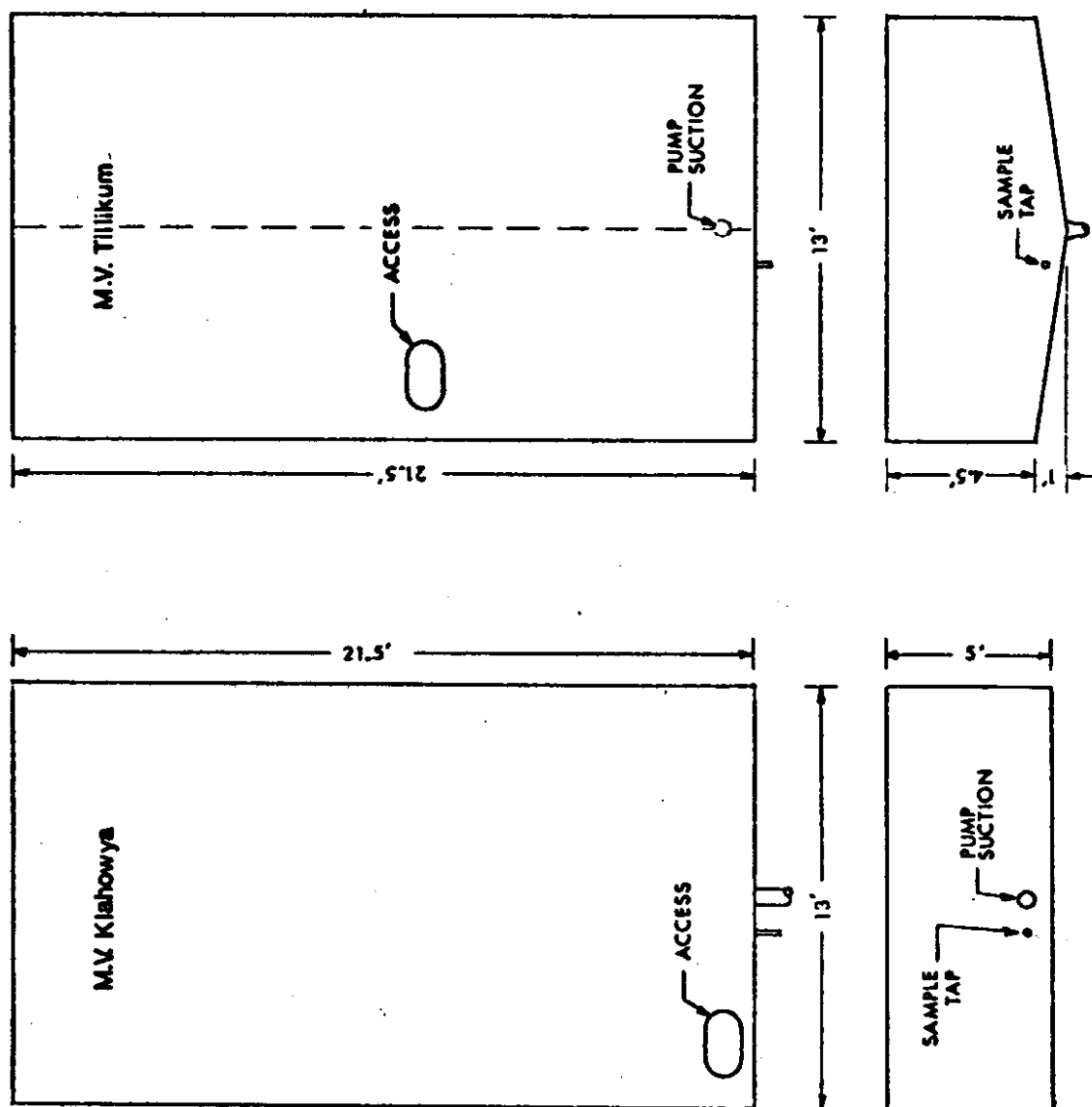


Figure 4. Approximate study vessel holding tank dimensions.

fide. Samples were removed from taps installed about six inches above the bottom of the holding tanks. Detailed procedures including sample preservation and analytical methods are presented by Browne, Ferguson and Sylvester (1976).

The results of waste characterization studies performed on 15 samples collected from the M. V. Tillikum and M. V. Klahowya between May 11 and August 5, 1976 are shown in Table 3. The results are based on samples of widely varying conditions of ferry traffic.

Variability

The most obvious conclusion to be drawn from the results is the large variability of characteristics as indicated by the coefficient of variation (standard deviation $\div$ mean) shown in Table 3. The highest variability is apparent in those parameters normally associated with sewage strength (BOD, COD, Suspended Solids). Those parameters primarily associated with seawater composition show lower coefficients of variability.

The concentration of dissolved sulfide in the samples showed the highest variability of all parameters. This is due to the high dependence of sulfide concentration on sewage age as will be discussed later in this report.

Although the analytical results did not show a significant difference between the character of the waste on the two study vessels with respect to most of the parameters, there was a significant difference in sulfide concentrations. The average sulfide concentration for samples from the M. V. Tillikum was 5.8 mg/l while the average for samples from the M. V. Klahowya was only 0.5 mg/l. This difference may be due to the daily scheduled pumping of the Klahowya tanks as opposed to the three times weekly pumping of the Tillikum. The extensive addition of E-Clor, a commercial odor control agent, aboard the Klahowya prior to the study period may have also had some residual effect

Table 3
Waste Characterization Results

Parameter	Units	Average	Minimum	Maximum	Coef. Variation
Total BOD ₅	mg/l	170	108	313	0.36
Filtered BOD ₅	mg/l	110	65	188	0.36
Total COD	mg/l	1000	467	1688	0.39
Filtered COD	mg/l	700	263	1513	0.50
Total Organic Carbon	mg/l	80	50	125	0.32
Suspended Solids	mg/l	230	89	531	0.50
Vol. Suspended Solids	mg/l	170	83	348	0.43
Chloride	g/l	17.0	15.2	19.0	0.07
Sulfate	g/l	2.4	1.8	2.8	0.08
Total Phosphorus	mg/l	7.0	5.9	9.3	0.21
Calcium	mg/l CaCO ₃	850	317	1134	0.27
Total Hardness	mg/l CaCO ₃	4800	4029	5397	0.10
Kjeldahl Nitrogen	mg/l N	80	49	102	0.20
Ammonia Nitrogen	mg/l N	76	39	94	0.21
Volatile Acids	mg/l Acetic Acid	70	19	130	0.41
Alkalinity	mg/l CaCO ₃	500	345	920	0.44
pH	-	8.2	7.5	8.9	0.06
Sulfide	mg/l	4.0	0	14.5	1.18
Spec. Conductance	$\mu\text{mho/cm}^2$	3.5×10^4	2.95×10^4	3.98×10^4	0.11

although bottle studies reported later in this report indicate that the agent was not very effective at the dosages used.

General Composition

The results shown in Table 3 indicate a waste strength comparable to domestic sewage with the constituents of seawater superimposed. The average salinity of the seawater during the summer near Vashon Island is about 29 parts per thousand (Collias, et al., 1974). Compared to the composition of this seawater, the concentrations of calcium, magnesium, sulfate and chloride indicate that the waste is about 90% saltwater derived from the seawater flushing systems on board. The remainder of the water in the waste is fresh water from wash basins, drains serving the galley, and crew's showers.

There is an apparent discrepancy between the values of BOD, COD, and TOC. The COD values indicate a higher strength waste than either the BOD or TOC. This may be due to several factors. The presence in the anaerobic waste of nonbiodegradable reduced species which are oxidized by the COD digestion may account for part of this difference. Oxidation of chloride in the COD test may also account for high values. Toxic effects causing low BOD values could account for the difference although different BOD dilutions which usually show different values under toxic influence, showed no indication of such toxicity.

The results indicate that the pH is consistently within the optimum range for sulfide production as determined by Pomeroy and Bowlus (1946). Also, the seawater portion of the waste provides an abundant supply of sulfate ion available for bacterial reduction to sulfide.

The average values indicate that 95% of the Kjeldahl nitrogen is in the form of ammonia. This may indicate that the majority of the nitrogen input is in the form of urea, a constituent of urine, which is rapidly hydrolyzed

to ammonia by enzymatic action. Organic nitrogen in fecal material is primarily associated with proteins which decompose slower. Therefore, the ratio of urine to fecal material is possibly higher in ferry waste than in normal domestic waste.

It is probable that because of the settling in the tank, the sampling method failed to obtain a representative fraction of the waste solids. If these solids were included, the data would probably indicate a higher proportion of organic nitrogen. A higher waste strength, as indicated by total BOD₅, COD and suspended solids, would also result.

Rate of Waste Accumulation

Figure 5 shows the result of on-board measurement of the generation of sulfide and wastewater volume during two summer weekdays. Measurement of tank volume indicates that the highest inflow is during the morning and evening rush hours although the changes are relatively small. Measurements of tank volume during other on-board tests (discussed later) indicated even less fluctuation of influent flowrate during the day. All of the tests were performed during the summer when tourist traffic will tend to dampen hourly fluctuations. The fluctuations may be more pronounced during the winter season, though the waste flows would probably be lower.

The data shown in Figure 5 represent the slowest accumulation of waste of all the on-board measurements taken. The average rate of accumulation during the period when the vessel was operating was 90 gallons per hour equivalent to about 1.0 gallons per passenger based on Washington State Ferries traffic data. The average rate of all the runs measured was 145 gallons per hour equivalent to about 1.8 gallons per passenger. The maximum rate measured was on September 22-23 with 270 gallons per hour or 2.8 gallons per passenger.

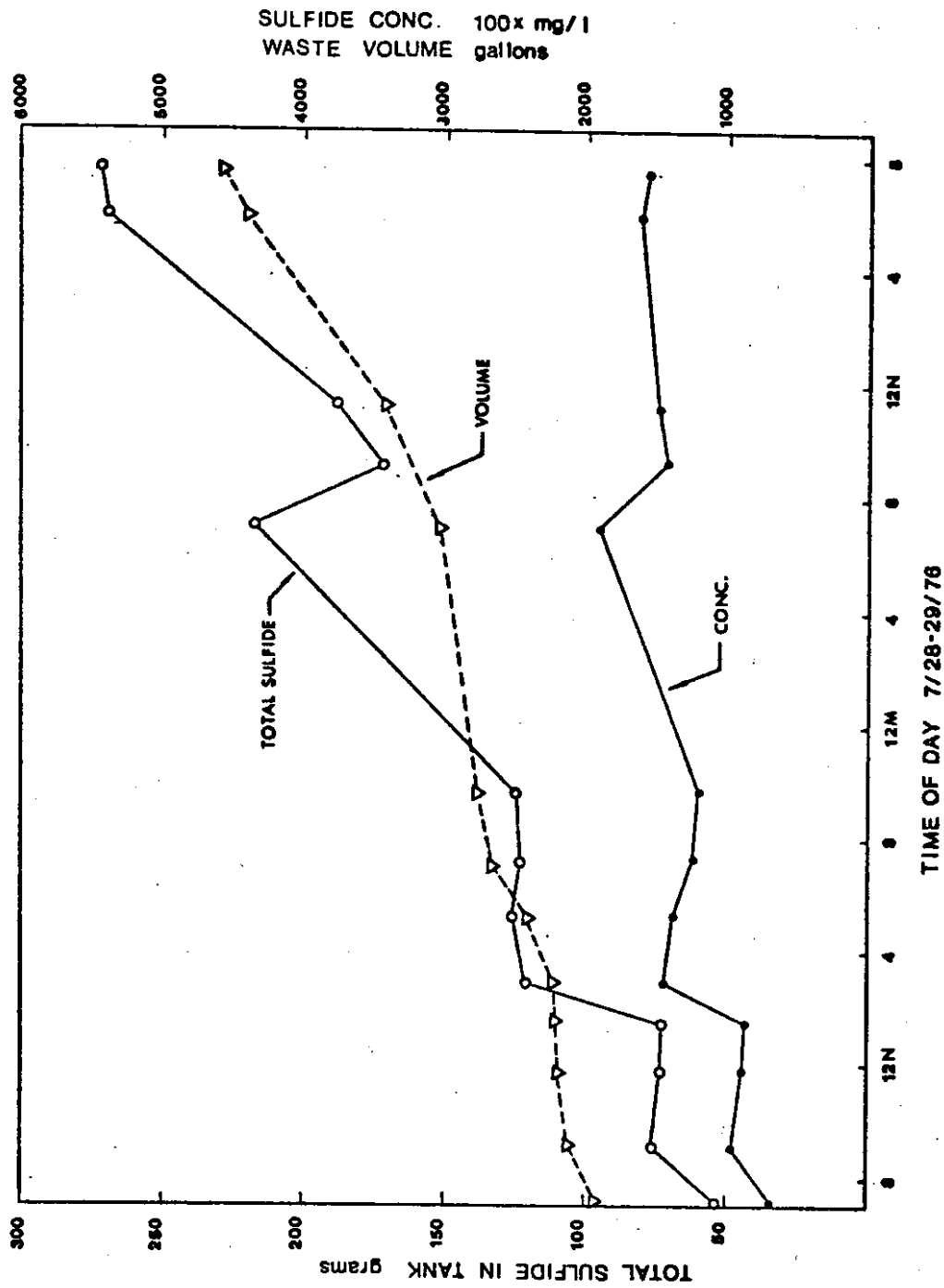


Figure 5. Wastewater sulfide and volume accumulation in M. V. Tillikum holding tank. No chemical addition.

Sulfide Generation Rate

As sulfide is generated in the holding tank, sulfide concentrations may not show the same increase as sulfide mass due to dilution by incoming waste. Figure 5 shows both the sulfide concentrations and the total mass of sulfide present in the tank as a function of time.

The total sulfide present shows considerable variation, probably mostly due to sampling errors. A linear regression analysis indicates that the average rate of sulfide production is 5.72 grams per hour. The rates measured during further on-board tests varied considerably, ranging from 4 to 17 grams per hour with one test much higher at 45 grams per hour. The average production rate for all the tests was found to be about 14 grams per hour.

In terms of production per unit area of tank exposed to the liquid, the average production for the on-board tests was about $0.40 \text{ grams/m}^2\text{-hr}$. This rate is higher than the range of $0.06\text{--}0.13 \text{ grams/m}^2\text{-hr}$ found by Pomeroy and Bowlus (1946) in flowing sewers at a temperature of 20°C with a waste of approximately 100 mg/l BOD.

The rate of sulfide production (grams/hour) in the tests shown on Figure 4 appears to remain relatively constant during the filling cycle. Since the area of the wall surface exposed to the liquid changes only slightly, it can be hypothesized that the bulk of sulfide production occurs in the wall slimes and sludge deposits. If production was dependent on wastewater volume, the generation rate would increase as the tank fills.

The specific rates based on wastewater volume range from 3.7 mg/l-hr at the start of the filling cycle to 0.46 before the tank was pumped, based on the average rate of sulfide generation (14 grams/hr) and average volumes from the on-board tests. The values consistently decline as the tank fills.

The specific volumetric rates may be compared to the rate of sulfide production measured in bottle test samples which ranged from 0.08 to 0.52 mg/l-hr averaging 0.33 mg/l-hr. Since the bottle test generation rates are lower and more constant than the rates in the tank, there is further indication that a large portion of the sulfide generation occurs in the wall slimes and sludge deposits which were not present during the bottle tests.

Conclusions

The ferry waste was found on the average to be similar to domestic waste in strength with the addition of the components of seawater present. The concentrations were much more variable than domestic waste, reflecting the unique characteristics of waste generation from varying passenger loads during the day with time aboard a vessel varying from 1/3 to 1 hour. There was also reason to suspect that the samples were affected by sedimentation of solids prior to sampling. It seems likely that concentrations of total BOD and COD, Kjeldahl nitrogen, suspended solids and volatile suspended solids all are significantly lower than actually introduced to the holding tanks.

V. Odor Control Alternatives for Sewage Holding and On-Shore Discharge

During the study as many as sixty alternatives or combinations were considered including physical, biological and chemical means of preventing sulfide generation and removing or immobilizing sulfides that were produced. Twelve were evaluated in detail with feasibility and costs assessed for the Evergreen State Class vessels. Five were subjected to laboratory and field trials, and three alternatives - hydrogen peroxide addition with or without recycle mixing and aeration with compressed air injection into a recycle line - met all technical criteria at low annual costs. These results are presented in this section. The studies of the recommended methods are presented in detail; studies of other alternatives are summarized to present the pertinent considerations which led to their final rejection. One option, conversion back to direct overboard discharge was considered and abandoned during the study. Since this option is not explicitly for odor control in the context of this chapter, the considerations and conclusions are described briefly in Appendix 1.

Specific criteria for the alternatives were developed to meet the general objective of controlling odors and related problems on board the vessel, in the vicinity of the terminal during discharge, and in the sewerage system.

1. The sulfide concentrations should be less than 0.5 mg/l in the holding tank contents at all times during the filling cycle and pump out. This level may be associated with faint, noticeable but not strong, odors (Figure 2). This represents about a 90% reduction from 4 mg/l average concentration observed in holding tanks. Most options should produce a level near zero mg/l.

2. The method should be uniformly applicable on all vessels on all runs.

3. The method should be operated by present crews with little or no change in the work load or duties.

4. The method should not require routine analytical testing or frequent operating adjustments. It should perform equally well in high or low load

periods, in winter or in summer.

5. The method must be economical. No firm criteria were available, but as a reference point the cost of the odor control chemical in use at the start of the study was approximately \$800 per vessel each year.

6. The method should have no adverse effects on the on-shore sewerage facilities.

In the following sections, three basic alternatives, conversion to fresh water, chemical treatment and aeration, are discussed with several chemical methods and aeration procedures individually considered. The mechanism by which each controls hydrogen sulfide generation or evolution is discussed along with its anticipated effectiveness with respect to the performance criteria. For the favorable methods, the results of testing to confirm feasibility and to develop dosage or operating requirements are presented.

Preliminary designs were developed for each method (Parrish, Ferguson and Sylvester, 1976) and the favorable ones are presented.

Cost estimates for equipment were prepared. Equipment is sized, operation is discussed, and flow diagrams are shown. Properties of chemicals, precautions for their use, recommended dosage, and the cost of that dosage are listed. The cost to operate new equipment, or existing equipment not presently operating in that service, is also listed.

Estimated installation costs should not be considered as absolute numbers, but rather, should be used to compare the relative cost for different alternatives, since estimates are based on the Evergreen State Class ferries. The amount of material required for each was based on a possible layout determined from visits to the M. V. Evergreen State and vessel drawings. These layouts may or may not be the optimum. Where possible, material prices were obtained from manufacturers or vendors. In other cases, cost indexes were used to update

prices of similar equipment. Prices are based on the list price and do not reflect discounts available to the State. Labor costs are based on data furnished by Nickum and Spaulding Associates, Inc., for shipyard labor rates (July, 1976).

Chemical costs are based on the dosage recommended for 10,000 gallons of wastewater. On runs where the wastewater generated is consistently less than this, the chemical use may be reduced accordingly. Usage is varied by adjusting the stroke on the feed pump and measuring the amount of liquid pumped. There is no measurement of chemical concentration in the wastewater, so if the rate is adjusted, it should be maintained at a rate high enough for proportionate dosage at the revised peak flow conditions. Prices used in the chemical cost estimates were supplied by manufacturers or sales representatives. No additional handling cost for the chemicals is included in the estimate since trucks presently deliver supplies to the vessels on a regular schedule.

Operating costs are based on the generator's fuel consumption per unit of power output. They are based on the average cost rather than the marginal cost. It is assumed that the existing electrical systems have enough excess capacity to supply the power required for any odor control method evaluated. Operating cost data were furnished by Nickum and Spaulding and are based on the type of generators used on the Evergreen State Class. Newer vessels may have more efficient systems. Operating costs are based on a regular timed cycle of intermittent operation to maintain adequate odor control.

All equipment has been designed to meet U. S. Coast Guard requirements for Marine Sanitation Devices. Chemical tanks have enough extra capacity to meet the rolling tests. Motors and electrical controls are also designed

accordingly. Chemical level indicators and alarms to indicate when chemicals must be added are provided. Pressure sensing devices are included to prevent over pressuring the sewage tank. Equipment is located to provide easy access for servicing. Materials used have been selected to meet the chemical resistance test.

A. Conversion to Fresh Water

If the major source of odor is hydrogen sulfide generated by the reduction of sulfate, then excluding the seawater sulfates will eliminate odor in the holding tanks. Sulfide buildup in sewers increases with increasing sulfate content of the wastewater (Thistlethwayte, 1972). Seawater contains 3.8×10^{-2} M/l SO_4 (3648 ppm) (Stumm, 1970), while fresh water in the Puget Sound region is usually below 10^{-4} M/l (10 ppm). However, organic wastes, particularly albuminoid protein with thioamino acids, add inorganic sulfur to the water as they decompose. Domestic sewage typically contains 1 to 3 ppm sulfur from organic compounds present in excreta (Thistlethwayte, 1972). Somewhat higher concentrations would be expected in ferry wastes since most of the flow is from the lavatories. While these organic sulfur compounds contribute to odor the major source is usually the reduction of inorganic sulfur compounds (EPA, 1974).

Replacing salt water with fresh water will reduce the sulfate content of the sanitary water system and limit the potential sulfide buildup, but it may not eliminate the odor problem. If all the sulfate present in fresh water was reduced to sulfide at neutral pH, 1-2 mg/l H_2S would result. With the partial decomposition of organic sulfur compounds, the corresponding atmospheric concentration would cause a definite odor problem. It is not expected that all sulfur will be converted to sulfide; however, depending on the residence time in the holding tank, there may be enough H_2S evolved to cause an odor problem.

Experience with sewage odor generation in the Puget Sound region and elsewhere suggests that short detention time in the holding tanks and thorough tank cleaning would be essential to prevent odors, even if seawater sulfate was eliminated. It probably would be necessary to revise the pumping schedule and to use some additional method of odor control in addition to converting to a fresh water sanitary system.

This alternative, then, is of questionable effectiveness; furthermore, a preliminary design was carried out that raised other technical and economic issues that led to its rejection.

Description of Fresh Water System

The existing fresh water storage tanks do not have the excess capacity required for sanitary water. A separate fresh water sanitary system with a new storage tank will be installed. The estimate is based on installing a 10,000 gallon water tank in the opposite shaft alley from the sewage holding tank. The basis for sizing the tank is one day's sanitary water requirement. The tank would be filled during the off hours.

New equipment for this system includes a 10,000 gallon fresh water tank (22.5 ft. x 13 ft. x 5 ft.) identical to the sewage holding tank and located in the No. 2 Shaft Alley. The interior of the tank is to be coated with coal tar epoxy. The tank will be provided with a level gauge and level alarm. This fresh water system is to be kept separate from the potable water system. New two-inch steel pipe fill lines will be provided from the No. 1 and No. 2 ends to the new tank. There will also be a vent and overflow line from the new tank. The existing salt water pressure tank and pump will be reused in this sanitary water system. A new two-inch line will be run from the new tank to the suction of the existing salt water pump. The ability to use salt water for sanitary water will be retained for emergency use.

The fresh water system has very high capital costs as well as the cost of purchasing additional fresh water. The estimated cost to install this system is \$38,500, and the cost of water based on the 1975 average price of \$.49 per thousand gallons assuming an average daily use of 6,000 gpd is \$2.94/day or \$1,073/year. Cost data are shown in Table 4. No significant change in operating expense is expected. No cost has been assessed for reduced vessel speed caused by the addition of the fresh water tank assuming that this will not require a change in schedules.

More frequent pumping may be required, which may involve schedule changes to accommodate the pumping schedule. The lag time before sulfide generation reaches an objectionable level may be increased if most of the sludge and slime can be removed from the tank (Baumgartner, 1934). This could be done by improved tank cleaning methods and installation of a bottom suction line and a recycle line at the sewage tank. These costs are discussed in Parrish, Ferguson and Sylvester (1976) but have not been included because of uncertainty about their effectiveness in this application.

Table 4 . Cost Summary Fresh Water

<u>Total Installation Cost</u>	\$38,500
<u>Water Cost</u>	
Based on 1975 average price of	\$.49/1000 gal.
Assume average daily consumption is	6000 gpd
Cost = 6000 gpd x \$.49/100 gal. = \$2.94/day = \$1,073/year	
<u>Operating Cost</u>	
No additional expense	
<u>Total Annual Cost</u>	
Including amortization of \$38,500 at 8% for 20 years = \$4,923/year	

B. Chemical Treatment

Chemicals can be used to reduce sulfide odors. Some inhibit the formation of sulfides by killing the sulfate reducing bacteria; others oxidize sulfides to sulfur or sulfate; others effectively reduce the concentration of H_2S (aq) by precipitating sulfides or by raising the pH and reducing the fraction present as H_2S ; others may mask the sulfide odor with their own characteristic odor. All of these possibilities were considered. The results for the infeasible chemicals are presented first.

1. pH Control

The fraction of dissolved sulfide present as hydrogen sulfide varies as a function of the pH of the wastewater. If the pH is maintained above 8.5, the amount of H_2S present is significantly reduced and the emission of hydrogen sulfide is virtually eliminated (Pomeroy, 1946; Thistlethwayte, 1972; EPA, 1974). At pH 9, the equilibrium concentration of dissolved H_2S is nil. Higher pH values (11-13) are toxic to the bacteria and control odors by preventing sulfide generation. However the higher pH values were found to result in large amounts of precipitate from sea water waste (Browne, Ferguson and Sylvester, 1976). The pH 9 level was used to compute costs for this method. This pH adjustment will eliminate the on-board odor problem as well as odor problems at the terminals when vessels are pumping wastes, but the amount of dissolved sulfide in the wastewater may be greater than at a lower pH because losses to the atmosphere are reduced. If at some point in the receiving sewer the wastewater from the ferries is mixed with water at a low pH, there will be a significant release of hydrogen sulfide gas, resulting in potential odor and corrosion problems at that location.

Several chemicals including lime and 50% liquid caustic were considered for use. It was decided that it was not practical to use lime because handling

the hygroscopic solids is very difficult. Conventional equipment for handling lime is too large for this application.

50% liquid caustic is available in 650 pound drums at a price of \$.18 per pound of NaOH. Based on laboratory tests to maintain pH 9, about 10 pounds of NaOH are required for 10,000 gallons of wastewater (Browne, Ferguson and Sylvester, 1976). The cost of this chemical dosage is \$1.80 per day or \$657 per year.

System design with cost estimates were made and showed no significant cost advantages compared to other options. Since there were potential odor and corrosion problems to the on-shore sewerage facilities, this alternative was dismissed in favor of those which would not yield adverse effects.

2. Precipitation of Sulfide with Iron Salts

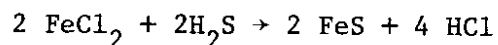
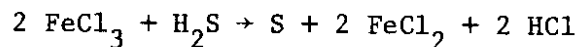
Metal ions may react with dissolved sulfide to form an insoluble precipitate preventing the escape of H_2S to the atmosphere. Iron, copper, and zinc salts have all been used for this purpose. Although zinc salts are commonly used to control odors in sewage holding tanks on recreational vehicles and pleasure craft, the mechanism is toxicity rather than precipitation of sulfides. This toxicity may carry over to the treatment plant receiving the sewage or to the water body receiving the treated wastewater. For this reason along with the high cost of these salts, iron appears to be the only suitable metal for this application.

Common forms of iron sulfides include FeS , Fe_3S_4 , and FeS_2 , so the theoretical iron requirements vary from 0.87 to 1.74 pounds per pound of sulfur (Thistlethwayte, 1972). The solubility product of ferrous sulfide (FeS), or pyrrhotite, is 6×10^{-18} (Bard, 1966), and a very slight stoichiometric excess of iron should result in low sulfide residuals at pH 9 or above. In actual practice a higher dosage is used to allow residual iron for additional sulfide

which may be generated in downstream sewers. The chemical dosage of 2.3 pounds of iron used in this estimate is based on precipitating 1.3 pounds (600 grams) of sulfide per 10,000 gallons of wastewater. A caustic dosage of 10 lb/day is also needed to maintain the pH at that for minimum FeS solubility. About the lowest dissolved sulfide concentration that is achieved is around 1 mg/l (Pomeroy, 1946; Thistlethwayte, 1972; EPA, 1974). Lower levels may be possible depending on the presence of dissolved oxygen in the wastewater.

The precipitation method does not meet the sulfide criteria of 0.5 mg/l; however since the pH will be increased to 8 or 10 the fraction of dissolved sulfide present as H_2S will be small. This method of treatment will not reduce the H_2S level to the odor threshold, but may approach the level of detection by the general public.

Both ferrous and ferric iron salts were considered for this application. Ferric salts are more effective under anaerobic conditions as is the case in the sewage holding tank (Pomeroy, 1946). Ferrous salts may increase sulfate reduction and sulfide generation. Ferric chloride was selected as the iron salt to be used; it reacts with sulfide according to the following reactions which produce solid sulfur and ferrous sulfide (Baumgartner, 1934):



The use of ferric chloride will not have any adverse effect on treatment plants receiving wastewater from ferries. Ferric chloride is commonly used in waste treatment for phosphate reduction, for sludge conditioning, and as a coagulant. The precipitated ferrous sulfide does not usually form scale and should cause no handling problems in the sewerage system.

This method of odor control may eliminate odor problems when the ferries are pumping waste ashore. If the sulfide level is low leaving the ferry, there

will probably be enough aeration in free flowing lines to prevent odor, and corrosion problems will be reduced because FeCl_3 removed H_2S .

Anhydrous ferric chloride is available at a cost of \$0.284 per pound. A solution should be prepared and fed frequently to the wastewater in the holding tank at a rate proportional to the rate of sulfide generation. A recycle system should be used to mix the iron dosage with the entire tank contents.

The system for using ferric chloride includes chemical tanks, feed pumps, holding tank recycle system, associated piping, valves, gauges and controls. The proposed system will use polyvinyl chloride (PVC) piping and a polyethylene mixing tank for handling 20% FeCl_3 solution. The chemical tank should be large enough to mix two drums of FeCl_3 . A diaphragm type chemical injection pump and spare with PVC heads will be provided for continuous injection of FeCl_3 solution. The injection line will be 1/2 inch PVC pipe. It should tie in to the recycle line downstream of the sewage pump to prevent any adverse effect on the sewage pump.

In addition a sodium hydroxide addition system similar to that envisioned for pH control will also be required. This system would include a caustic storage tank, feed pump, piping, gauges and related instrumentation. The base addition requirement would be similar to that required for pH adjustment without the iron salt. The cost of the base was previously estimated to be \$1.80/ day or \$657/year.

Also included in the estimate is a recycle line with four tangential nozzles. It is essential to this treatment method that the tank be adequately mixed so the iron and the sulfide can react.

Instrumentation will include a high level shut down of the water in the chemical tank. The tank will be equipped with a level gauge, a low level alarm, and a low level shut down of the injection pump. The injection pump will

also be shut down when the sewage pump is not operating thus insuring that there is a large flow of water to prevent the buildup of corrosive concentrations of FeCl_3 . Calibrated chambers will be used to measure the chemical flows.

The costs for this system are listed in Table 5. The estimated cost to install this system is \$19,090. Chemical costs, based on precipitating 600 g of sulfur are \$1.94/day for FeCl_3 and water (\$709 per year) and adding 10 pounds/day of NaOH at \$0.18/pound (\$657/year) are \$1,366 per year. Operating costs based on running the sewage pump and the chemical injection pump are \$2.34/day or \$850 per year. The total annual cost, based on amortization at 8% interest for 20 years, is \$4,125.

The method, which was not tested in the laboratory or on the vessels, is probably technically feasible for controlling odors. It is more effective than base addition by itself, but less effective than methods that either destroy the sulfide or prevent sulfide generation. The design showed that the method is complex and costly compared to others. The method is not recommended for use in on-board odor control.

Table 5. Cost Summary - Precipitation with Ferric Chloride Addition

Total Installation Cost	\$19,090
Annual Chemical Cost	\$ 1,366/year
1.32 pounds of sulfide are to be precipitated, requiring 6.82 lb./day ferric chloride @ \$0.284/lb.	
10 pounds of NaOH at \$0.18 per pound pumps 10 minutes each hour, 24 hours per day	
Annual Operating Cost	\$850/year
operate sewage and chemical feed pumps 10 minutes each hour, 24 hours per day	
Total Annual Cost	\$4,125/year
including amortization at 8% for 20 years	

3. Chlorination

Chlorination is one of the oldest methods of odor control. Chlorine is both a strong oxidizing agent and an effective disinfectant. If chlorine is added slowly to wastewater containing sulfide and mixed vigorously, sulfur will be formed according to the reaction: $\text{HS}^- + \text{Cl}_2 \rightarrow \text{S} + \text{H}^+ + 2\text{Cl}^-$ (EPA, 1974). The reaction is instantaneous and consumes 2.22 parts of chlorine per part of sulfur. If an excess of chlorine is added to wastewater containing sulfur, the sulfide is oxidized to sulfate: $\text{HS}^- + 4\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{Cl}^-$. This reaction may proceed at a slower rate (Chen, 1974). Theoretically, 8.87 pounds of chlorine are required per pound of sulfide, but in actual practice chlorine reacts with other compounds present in the wastewater and 10 to 15 pounds may be consumed (EPA, 1974). Factors that affect the relative amounts of sulfur and sulfate formed include pH, temperature, reaction time, concentration of reactants, rate of reactant addition, and initial mixing intensity (Chen, 1974).

While the above reactions are effective for controlling odor, chlorine addition has generally been more effective for bacterial inhibition than for sulfide oxidation. Chlorine doses have an inhibitory effect on sulfide producing slimes and also depress biological activity and stop oxygen consumption until the chlorine residual has disappeared. (Dague, 1972; Thistlethwayte, 1972; EPA, 1974). Chloramine compounds formed with ammonia in the wastewater will destroy additional sulfide and control bacteria (Weber, 1972). The environment of the slime growth and sludge deposits in the sewage tank is different than that in flowing wastewater. The high organic content of the sludges and slimes may consume the chlorine and protect the sulfate-reducing bacteria.

Slug addition was chosen over continuous injection since the effectiveness of disinfection depends on the exposure of the bacteria to a high concentration

of chlorine. Two systems for slug addition have been proposed by Parrish, Ferguson and Sylvester (1976). One system involves manual addition through a dosing line extending through the tank ceiling. A recycle line was included in the design to provide rapid mixing of the dose. The second system provides automatic injections of slug doses to a recycle line similar to that discussed previously.

Dosage and Application

The recommended chlorine dosage for disinfection of raw sewage is 6-25 mg/l (Metcalf & Eddy, 1972). However, only about 60% of this demand may be required to inhibit sulfate reducing bacteria. Ferry wastewater contains as much as 20 mg/l dissolved sulfide in a stagnant tank with sludge and slime on the bottom and walls. The key to odor control using this method will be to reduce the chlorine demand for sulfide oxidation by inhibiting sulfide generation. Tests were performed to determine the dosage required to accomplish effective odor control, both in the laboratory and on-board in the vessel holding tanks.

Bottle Tests

The results of a series of bottle tests are shown in Figure 6. The first bottle test used waste from the M. V. Tillikum which had a considerable sulfide content (5.8 mg/l). Doses up to 20 mg/l had little effect on the rate of production. The 30 mg/l dose slightly reduced both the generation rate and the concentration after two days and significant inhibition of sulfide generation was achieved with a 40 mg/l dose.

The amount of sulfide oxidized per part chlorine added varied greatly for the different doses. The addition of 10 mg/l as chlorine oxidized sulfide in the ratio of 4.4 parts chlorine per part sulfide oxidized. This ratio increases with increasing dosages to a value of 10.8 for the 40 mg/l dose. These values indicate that oxidation of sulfide to elemental sulfur, theoretically

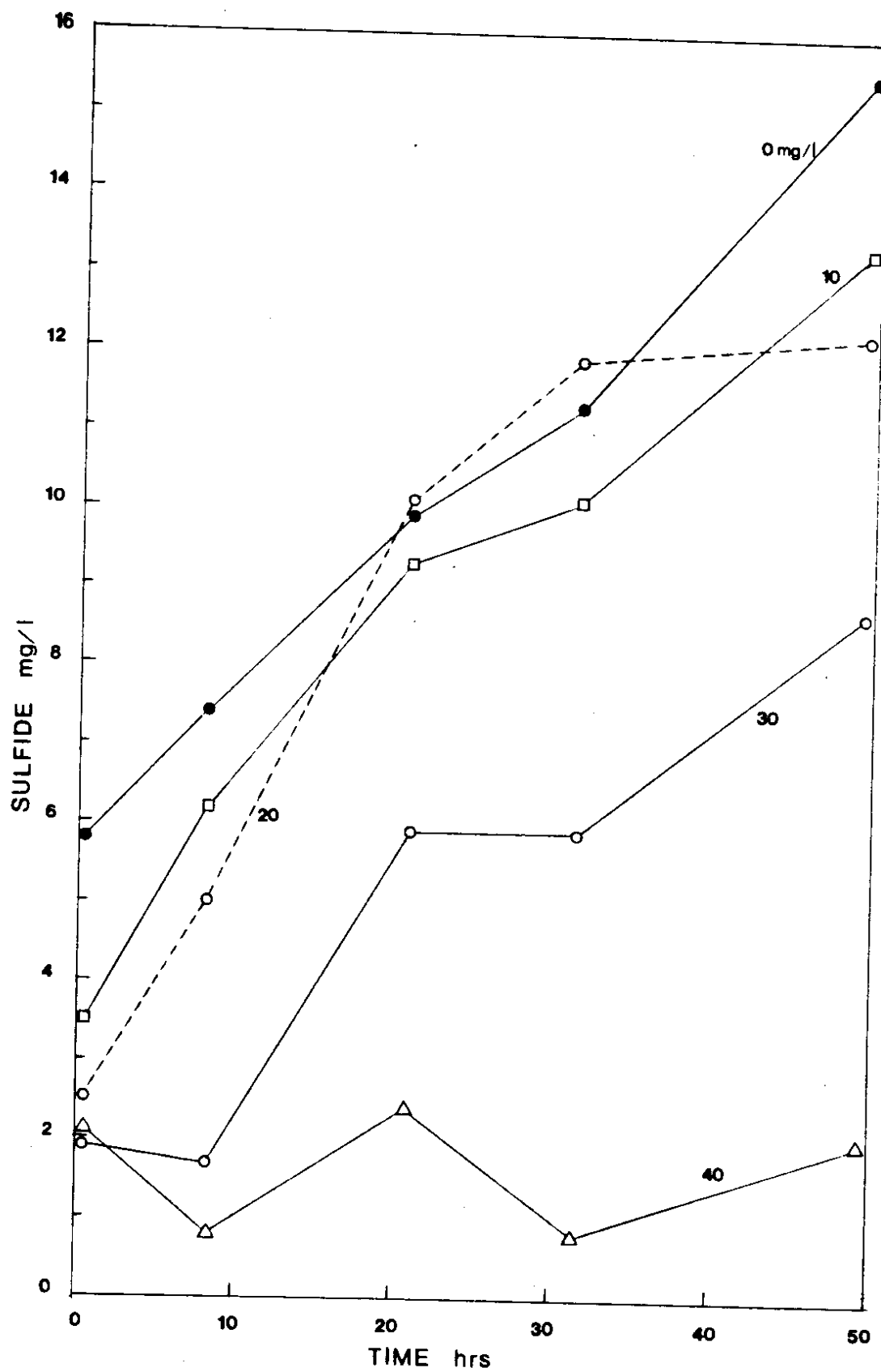


Figure 6 Sodium hypochlorite bottle test, 9/14-16/76.

requiring 2.2 parts chlorine per part sulfide, is prevalent at low dosages under these conditions. The further oxidation of sulfide to sulfate, which requires 8.9 parts per part, apparently does not predominate below the dosage of 40 mg/l. This conclusion is supported by qualitative observation of increased turbidity in the 10, 20, and 30 mg/l bottles compared to the blank and 40 mg/l bottles.

The rapid mixing and contact between the chlorine and the wastewater in the bottle tests and the low dosage of chlorine have been previously shown to support the partial oxidation of sulfide to elemental sulfur.

These results were consistent with the studies cited previously. A dosage of about 60% of the chlorine demand was effective in inhibiting sulfide production for several days. The question remaining was whether similar dosages could be used in the holding tanks to inhibit the bacteria in the slime and sludge and whether the dosages could gradually be reduced as sulfide levels and their chlorine demand were reduced.

On-Board Tests

On-board tests were made to evaluate the effectiveness of chlorine addition. Figure 7 illustrates the results of on-board Run 3.

During Run 3, the tank was mixed using a submersible pump and samples were taken directly from the main body of liquid in the tank. It was noted that the operation of the pump produced only minor turbulence but it did establish a circulation in the tank which at least slowly mixed the dosages away from the point of application.

There was a decrease in sulfide caused by chlorine oxidation that was detectable immediately after dosage. Doses of 43 mg/l (390 grams) and 48 mg/l (565 grams) resulted in sulfide oxidation at the ratio of 16 parts chlorine

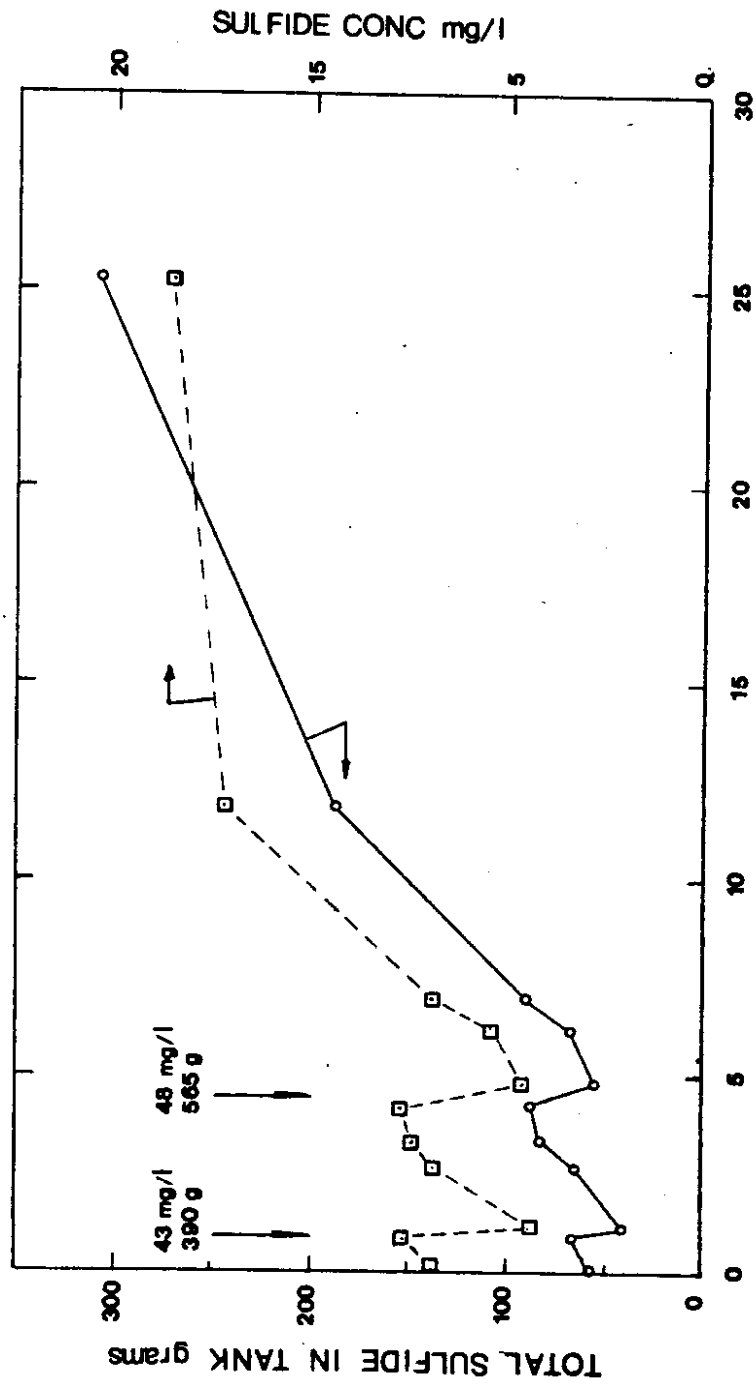


Figure 7 - Sodium hypochlorite addition to M.V. Tillikum holding tank, 8/20-21/76.

per part sulfide. Following this decrease, the generation of sulfide resumed in both cases at the rate of about 16 grams/hour. The doses in this run were greater than doses which had been found in bottle tests (Figure 5) to inhibit production of sulfide, yet no inhibition of sulfide production occurred. This is probably due to several factors including the presence of slimes and sludge deposits in the tank, the decreased mixing intensity in the tank, and the decreased efficiency of sulfide oxidation. All of these factors will decrease the contact of the chlorine with the bacteria causing less bacterial inhibition.

Much larger doses were added in a later run (Figure 8) and still no significant inhibition of sulfide production was evident. Chlorine demand tests were run during this test and a demand of 110 mg/l was measured prior to the first dose. Based on the theoretical chlorine requirement of 8.8 parts chlorine per part sulfide oxidized, the sulfide accounted for over 75% of the demand. The first dose at three hours of 70 mg/l (630 grams) was slightly over 60% of the measured demand. Sulfide oxidation occurred with a ratio of 21 parts chlorine per part sulfide removed and was followed by sulfide generation at the rate of 11 grams/hour, indicating little inhibition.

The second dose, at seven hours, of 80 mg/l (950 grams) was approximately equal to the chlorine demand measured prior to the dosage (although no chlorine residual was detectable immediately after dosage). Sulfide oxidation occurred at the same ratio as the first dose (21:1). The generation rate following the oxidation continued at about 11 grams/hour.

The third dose, at twenty-five hours, of 70 mg/l (1110 grams) caused a slightly less efficient oxidation of sulfide (26.5 parts chlorine per part sulfide), and no effects on the generation rate were detectable.

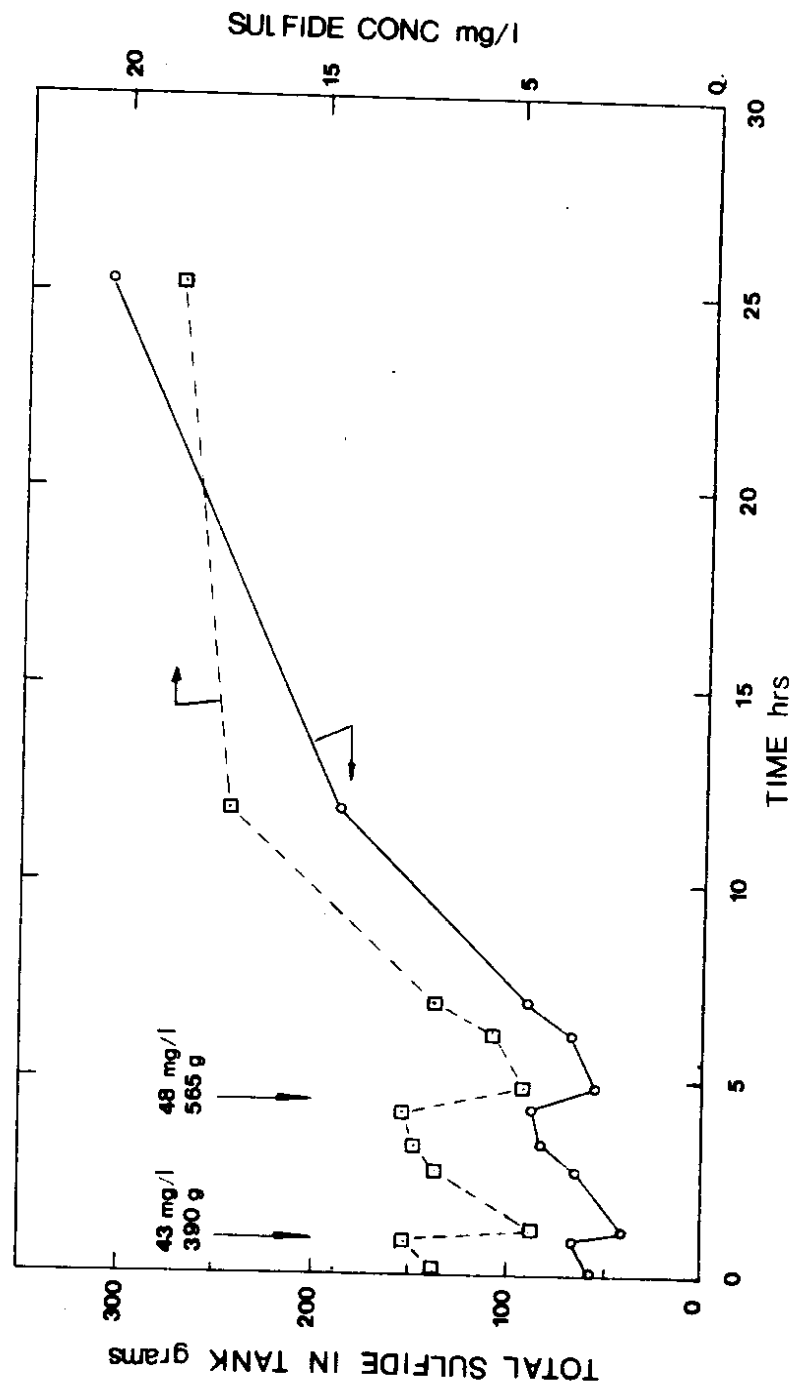


Figure 8. Sodium hypochlorite addition to M. V. Tillikum holding tank, 9/25-26/76.

Conclusions From Testing

The results of chlorination bottle and on-board tests indicated dramatically different degrees of success for odor control. The bottle tests showed more efficient sulfide oxidation and bacterial inhibition than did the on-board tests.

Sulfide oxidation in the bottle tests was found to occur at ratios of 4.4 to 10.8 parts chlorine per part sulfide oxidized. It was apparent that some oxidation of sulfide to sulfur (rather than sulfate) occurred with doses less than 40 mg/l yielding more efficient ratios.

On-board tests indicated much less efficient sulfide oxidation with ratios varying from 16 to 26.5 parts chlorine per part sulfide. This variation is probably due to poorer mixing and to the oxidation of reduced species present in wall slimes and sludge deposits. The bottle test doses were rapidly mixed with the waste causing rapid contact between the chlorine and the sulfide. Only a small degree of mixing was provided in the holding tank by the pump used in the on-board tests.

Based on the bottle tests and previous studies (Heukelekian, 1942), it was expected that dosages of a fraction of the chlorine demand would inhibit the sulfide producing bacteria. After a series of such dosages the chlorine demand from sulfide would be reduced even further. The findings were instead that repeated dosages near the chlorine demand did not inhibit the sulfide producers. The tests were conducted in a holding tank with minimal sludge accumulation, so we conclude that the slime layers protected the sulfide producers from inhibition by the chlorine.

The use of chlorine might be made to work by using higher chemical dosages than those tested and by improving tank cleaning procedures, especially on

vessels that can accumulate sludge layers. There was no evidence in the on-board tests that any of the tested dosages were effective. Hence the required dosage is indeterminate, but probably very high.

System Design

Designs were produced for chlorine addition for either manual batch addition to the holding tank or for addition to a recycle line which would insure good mixing. The batch addition alternative is described briefly.

Although chlorine can be applied to wastewater in several forms, it was concluded that a liquid solution of sodium hypochlorite (NaOCl) was most appropriate for this application.

For the case of manual addition, sodium hypochlorite would be added through a one-inch fill line from a convenient location above the high level in the sewage tank.

To provide mixing of the hypochlorite solution and the wastewater, a recycle line as described previously will be provided. While it is not necessary that the sewage pump be run continuously - one-half hour should be adequate for tank mixing - the tank may be kept cleaner if the pump keeps it circulating (Bhatla, 1975). The cleaner the tank is, the more effective the chlorination treatment will be, and less chemicals will be required. The estimated cost to install this system is \$6,250. The chemicals are indeterminate. The cost basis for a 40 mg/l dosage each day is an annual cost of \$1,504 per year. Operating costs would be about \$400 per year if the sewage pump is used only for mixing four times per day. These costs are summarized in Table 6.

Table 6. Cost Summary for Chlorination with Sodium Hypochlorite

Manual Batch Addition

Total Installation Cost	<u>\$6,250</u>
-------------------------	----------------

Chemical cost cannot be estimated since an effective dosage was not found. The cost basis for a chlorine dosage at 40 mg/l in 10,000 gallon tank is as follows:

2.64 gallons of NaOCl solution required. Sodium hypochlorite in 1 or 5 gallon containers cost \$1.55/gallon.

Cost = 2.64 gal x \$1.55/gal = \$4.12/day or \$1,500/year.

Operating Cost

Sewage Pump 15 Hp 30 minutes, 4 times/day	\$1.10/day
---	------------

\$400.00/year

4. Commercial Odor Control Compounds

Odor suppressing compounds sold for use in chemical toilets (holding tank and circulatory types) are diverse in their chemical nature, but usually contain, in addition to a bacteriostatic agent, an odor masking compound or perfume and a dye. The bacteriostatic agents used range from chlorinated hydrocarbons (ortho-dichlorobenzene in E-Clor) and formaldehyde to zinc salts. There are also proprietary formulations that use unspecified active ingredients.

The chemicals are usually expensive, from \$5.00 to \$15.00 per gallon, and may require dosages from tens of ppm to thousands of ppm for effective odor control. The chemical costs of using these compounds ranges up from \$2.25/day per vessel (recent use of E-Clor) to perhaps \$20.00 - \$50.00/day for effective control using a biodegradable formulation.

The most commonly used toilet additives have ingredients of zinc or formaldehyde, the most common zinc salt is zinc sulfate. Formaldehyde is usually present as formalin (aqueous) or paraformaldehyde(solid). Recommended dosages result in concentrations of zinc sulfate ranging from 1500 to 4400 mg/l. Biological treatment of wastewater by the activated sludge process will be significantly disrupted by zinc concentrations greater than 20 mg/l or formaldehyde concentrations above 120 mg/l (Robins, 1974). Additives containing formalin are toxic at lower concentrations than those using solid paraformaldehyde.

Commercial odor suppressing compounds also contain other chemicals in addition to bacteriostatic agents. Dense dyes and perfumes are used to mask offensive colors and reodorize the wastewater. Methylene blue, used as a dye in some additives, has a definite toxic effect on most bacteria. Surfactants and water softeners are added to solubilize the waste solids.

In the following section, there is a discussion of the use of chlorinated hydrocarbon compounds, such as E-Clor, the odor control compound which has been used until 1977 by the Washington State Ferries. Use of these compounds and of metal containing compounds is not acceptable based on the toxicity of the compounds to waste treatment processes and on poor removal of the compounds with possible effects on aquatic life after discharge of the sewage effluent.

Mechanism and Effectiveness Chlorinated Hydrocarbons

Chlorinated hydrocarbons were developed to exhibit toxic properties over an extended length of time. Many persistent insecticides and herbicides such as DDT, Chlordane, and 2,4,D are chlorinated hydrocarbons. The chemical recently added to the sewage tanks, E-Clor, contains dichlorobenzene, a chlorinated hydrocarbon.

Chlorinated hydrocarbons control sulfide odors by inhibiting sulfide generation rather than by oxidizing sulfide. In fairly fresh sewage they can reduce sulfide generation by up to 75% (Eliassen, et al, 1949). This reduction is not as effective as chlorine and probably is not adequate for odor control. Increasing concentration does not appear to further decrease the sulfide generation significantly. When sewage becomes anaerobic and septic with sulfate reducing bacteria present, chlorinated hydrocarbons exhibit only small inhibition of sulfide generation. It appears that chlorinated hydrocarbons have a significant effect on facultative bacteria with less on anaerobic sulfate reducing bacteria. By inhibiting the facultative bacteria which consume oxygen the chlorinated hydrocarbons may extend the time that aerobic conditions are maintained and delay the evolution of hydrogen sulfide gas.

To control sulfide generation, chlorinated hydrocarbons must be added before the sewage becomes septic. If the sulfate reducing bacteria, Desulfovi-

brio desulfuricans, are already present in large numbers in the slime and sludge, the treatment will not be effective even if the chemicals are added in time. In order for treatment with chlorinated hydrocarbons to be effective, Desulfovibrio desulfuricans must be killed with chlorine or all sludge and slime must be removed from the sewage tank and the tank kept clean by proper washing procedures. Small dosages of chlorinated hydrocarbons will prevent sulfide generation from organic sulfur containing compounds. However, most sulfide in salt water sewage is produced by the reduction of sulfate by Desulfovibrio desulfuricans under septic conditions which nullify the inhibitory effect of chlorinated carbons. Sulfate reduction, per se, is not controlled effectively by the use of chlorinated hydrocarbons (Eliassen, et al., 1949).

Due to the toxicity of chlorinated hydrocarbons to many life forms, the discharge of such compounds to municipal sewage systems has been considered undesirable. The Municipality of Metropolitan Seattle has listed chlorinated hydrocarbons among prohibited substances for discharge to their system. These compounds are often not significantly removed by sewage treatment processes, especially primary treatment which is still common in Puget Sound coastal communities. The compounds may be released to receiving waters where continued toxicity may affect the aquatic community. Toxic effects may also adversely affect biological treatment processes, although concentrations from ferry discharges would likely be low due to dilution.

Significant toxic effects of chlorinated hydrocarbons have been shown on aquatic life. Palmer and Maloney (1955) found chlorinated benzenes to be toxic to a variety of algal species at a concentration of 2 mg/l. McKee and Wolf (1971) quote studies which show chlorinated benzenes to be toxic to fish in concentrations ranging from 3.2 to 100 mg/l. Impedance of oxygen uptake at the gills of fish has been proposed as the toxic mechanism.

At subtoxic levels, chlorinated hydrocarbons tend to be accumulated in fatty tissues of aquatic organisms and may pose toxicity problems to consumers of these organisms (Weber, 1972). These accumulations can be released rapidly when the stored fat is called upon as an energy source (Rudd, 1964).

The handling of chlorinated hydrocarbon compounds can pose a significant health hazard to crew members. Ortho-dichlorobenzene is an irritant to skin and when vapors are inhaled, causes mucus membrane irritation (Sax, 1968).

Due to these problems, the use of E-Clor was thought to be undesirable. One bottle test was performed to evaluate the effectiveness of E-Clor since a very high effectiveness could possibly justify continued use.

Bottle Test

Figure 9 shows the results of a bottle test measuring sulfide generation in the presence of various doses of E-Clor. Sulfide generation was reduced by a dosage of 60 mg/l, a dose of 40 mg/l had a slight effect and lower doses had no effect. This dosage level is approximately equal to the required dose of hydrogen peroxide required to achieve inhibition of sulfide generation. The concentration is about ten times the manufacturer's recommended dosage for its intended application in sewage treatment plant (Pace Chemical Co.). Doses up to 60 mg/l showed no removal or reduction of sulfide present in the waste prior to dosage. The chemical cost of a 60 mg/l dosage in 10,000 gallons of wastewater is approximately \$1,100 per year based on a cost of \$6.00 per gallon for E-Clor.

In the holding tanks, the continued application of small doses may be somewhat effective if the E-Clor accumulates in the slime layers and eventually becomes toxic to the sulfate reducing bacteria. It is noted that considerable sulfide odor has been found during discharge of ferry waste from vessels regularly adding E-Clor in doses of approximately 50 mg/l. Measure-

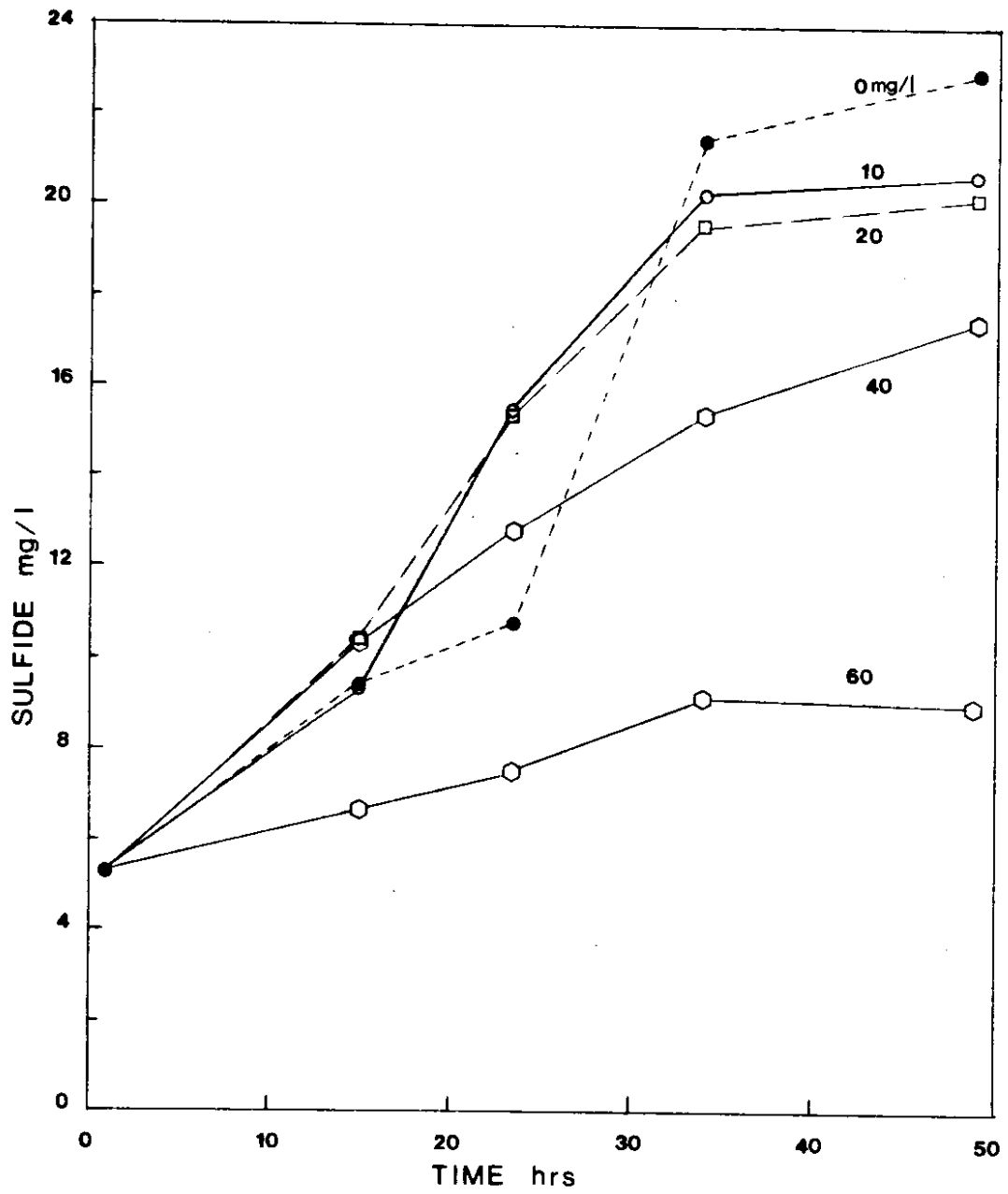


Figure 9 - E-Clor bottle test, 9/17-19/76.

ments of ferry waste pumped from the M.V. Elwha, upon entering the Edmonds sewage treatment plant, showed a sulfide concentration of 8 mg/l after a three-fold dilution by the municipal waste despite the addition of E-Clor. Measurements in the M.V. Tillikum holding tank during a period of E-Clor use showed an average of 3.3 mg/l sulfide.

Conclusions

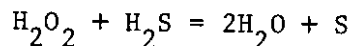
The use of persistent toxicants for odor control has been shown to be generally undesirable. The costs are generally high, ranging from \$5 to \$15 per gallon with uneconomical dosages needed. Other potential problems include toxicity to biological waste treatment processes and to aquatic life and toxic effects to crew members.

Tests on one compound, E-Clor, have shown it to be ineffective in sulfide oxidation. Sulfide generation rate was inhibited by a dose similar to that required for hydrogen peroxide addition, and the chemical costs are approximately double with E-Clor.

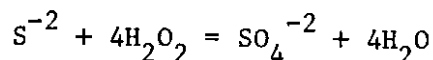
These factors indicate that the use of these compounds is an undesirable alternative and that there is no benefit great enough to justify their use in the face of the undesirable effects.

5. Hydrogen Peroxide as an Oxidant and Bacteriocide

Hydrogen peroxide (H_2O_2) has been used successfully to combat hydrogen sulfide odors from force mains, pumping stations and sewage treatment plants (Cole, 1976 FMC Corp; & EPA, 1974). Hydrogen peroxide reacts with hydrogen sulfide to form water and colloidal sulfur at near neutral pH ranges.



At higher pH values, 8.5 to 9.0 and above, sulfide is oxidized to sulfate.



The former equation is probably most representative of the reaction in this system. Stoichiometrically this reaction requires a 1:1 mole ratio of hydrogen sulfide and hydrogen peroxide. However, in actual practice, two to three times as much hydrogen peroxide are required due to other compounds present in the wastewater (FMC Corp.).

Slug additions have been found to inhibit the generation of sulfides. Hydrogen peroxide is toxic to bacterial slimes and will inhibit their growth. Most bacteria produce hydrogen peroxide in the presence of free oxygen, and nature has provided the enzyme catalase to decompose hydrogen peroxide to water and oxygen (Weber, 1972). Organisms that can produce catalase are able to avoid destruction until the applied hydrogen peroxide exceeds their enzyme production. Because of this, a hydrogen peroxide dose of 30 - 50 mg/l is recommended to inhibit slime growth (Cheremisinoff & Young, 1975). Many anaerobic bacteria, including the sulfate reducers, lack catalase and may be killed by lower dosages of H_2O_2 .

The odor control effectiveness of hydrogen peroxide addition was evaluated using laboratory tests to find dose response for sulfide oxidation and inhibition. On-board tests were also conducted to confirm effectiveness and evaluate the use of slug peroxide addition with minimal tank mixing.

Laboratory Bottle Tests

In Figure 10, bottle test results show that doses of 40 mg/l and over resulted in lower sulfide concentrations after two days than the initial concentration. Although considerable variability is apparent, a dosage of 60 mg/l shows definite inhibition of renewed sulfide production over the two-day period.

The oxidation of sulfide based on the initial measurements required ratios of between 6.5 and 20 parts peroxide per part sulfide oxidized. These ratios are much higher than the values of 2-3 given in the literature. This discrepancy is probably due to the insufficient time (about 15 minutes) allowed for completion of the oxidation reaction between dosing and initial sampling. The lower sulfide concentrations after 9 hours supports this contention. The ratios, based on the 9 hour sulfide concentrations, were lower than the initial ratios but were still high, ranging from 7 to 14 parts peroxide per part sulfide. It appears likely that the 40, 60, and 80 mg/l doses all reduced the sulfide level to near zero following completion of the oxidation reaction.

On-Board Tests and Field Monitoring

Two on-board tests of hydrogen peroxide addition were made in Autumn, 1976 while wastewater temperatures were high. Monitoring studies were also performed in early 1977 when hydrogen peroxide was used on all vessels. The results of these studies verified the feasibility of slug peroxide addition and refined the system of chemical mixing and feeding described subsequently.

One on-board test (Figure 11) involved two doses of peroxide. The first dose of 20 mg/l (180 grams) resulted in rapid oxidation of sulfide over a one-hour period followed by renewed generation. A dissolved oxygen concentration of 1.5 mg/l was measured two minutes after dosing and the

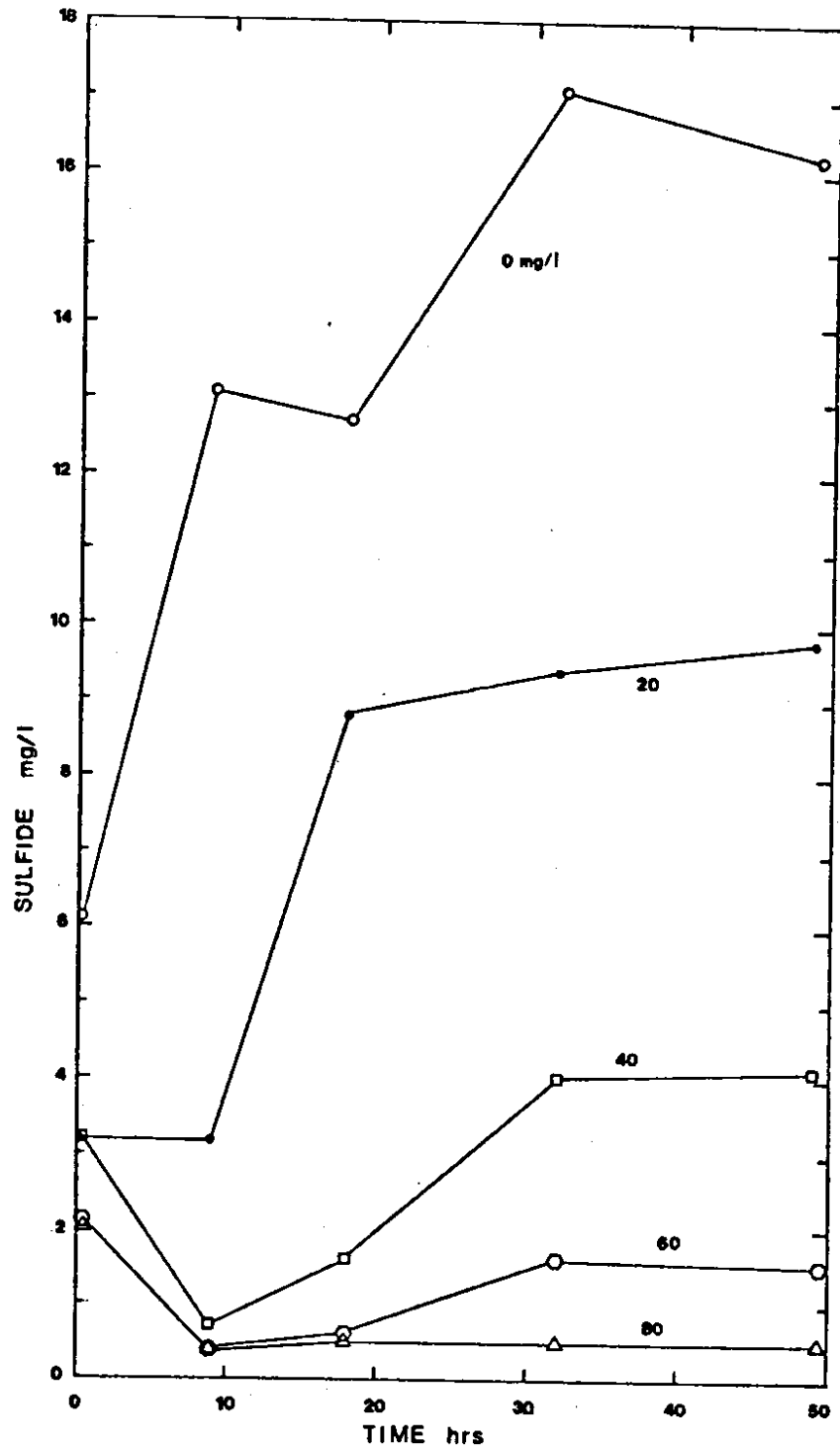


Figure 10 Hydrogen peroxide bottle test, 9/17-19/76.

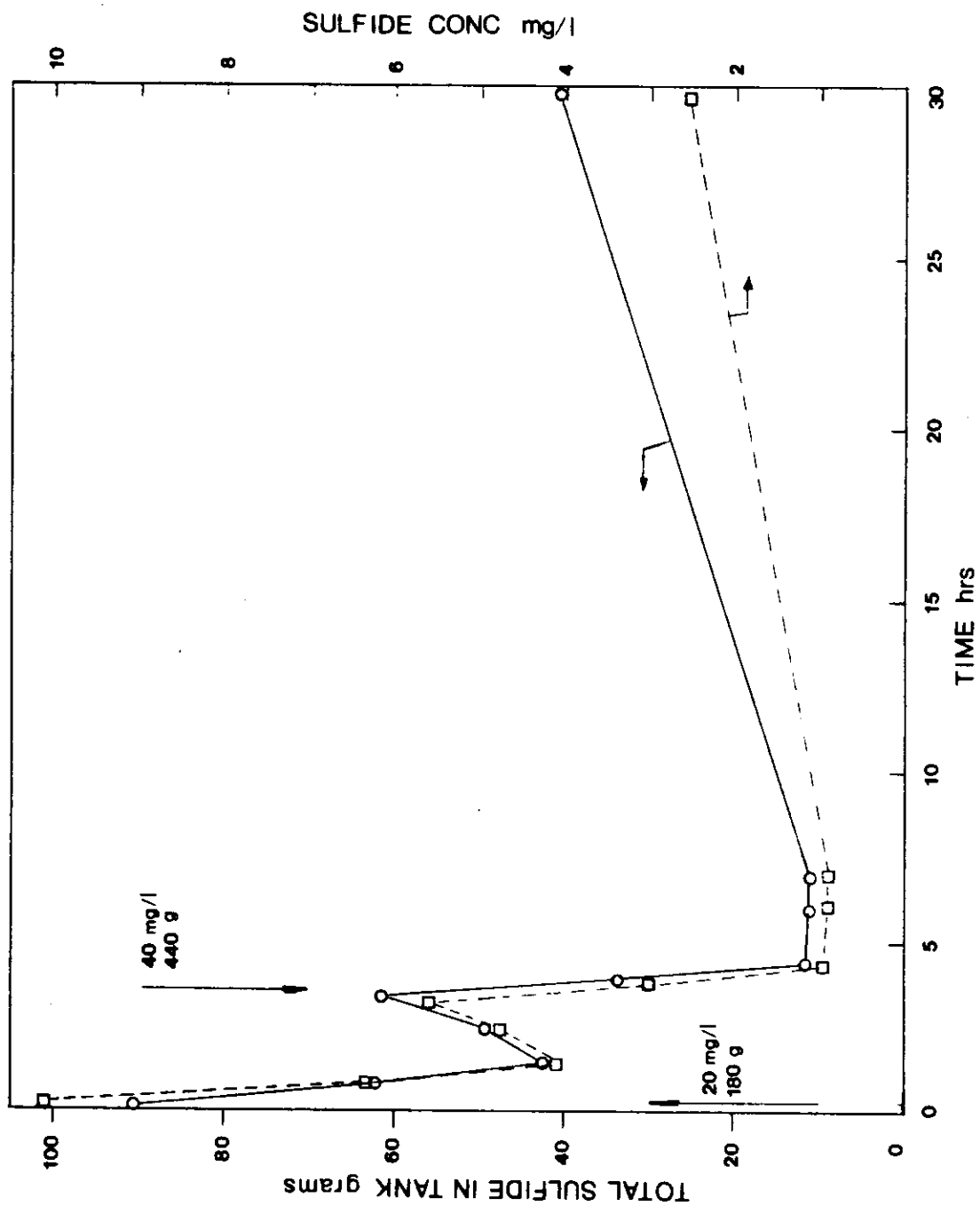


Figure 11. Hydrogen peroxide addition to M.V. Tillikum holding tank, 9/28-29/76

level remained over 1 mg/l for about 15 minutes. The oxidation required 3.7 parts peroxide per part sulfide. Due to the length of time required for the sulfide to reach a minimum level and the rapid occurrence of dissolved oxygen in the waste, it is likely that a portion of the decrease was due to sulfide oxidation by oxygen released rather than peroxide. A rapid regeneration of sulfide over the next two hours at a rate of 10 grams/hour occurred. The next dose of 40 mg/l (440 grams) reduced the sulfide concentration to under 1 mg/l with a hydrogen peroxide to sulfide ratio of 8.8. Dissolved oxygen was present in the tank above 3 mg/l for over two hours, during which no regeneration of sulfide occurred. Although insufficient data was collected in the following time period, it appears that the rate of renewed sulfide generation was greatly reduced by this dose.

A dosage of 65 mg/l (1500 grams) (Figure 12) showed a similar rapid reduction of sulfide level with an identical ratio of hydrogen peroxide added to sulfide oxidized as noted for the 20 mg/l dose (3.7). Regeneration of sulfide was stopped for at least 7 hours during which time dissolved oxygen concentrations remained over 1.0 mg/l and sulfide concentrations were consistently below 1 mg/l. Some regeneration of sulfide occurred during the next 17 hours but sulfide concentrations remained below 2.5 mg/l.

The tests indicate that effective sulfide control can be achieved by the mechanisms of bacterial inhibition and sulfide oxidation. In on-board tests sulfide was oxidized by the addition of 3.7 parts peroxide per part sulfide. Inhibition of microbial sulfide generation was an important result of repeated or fairly high hydrogen peroxide dosages.

Throughout a three month monitoring period, chemical additions were applied to the wastewater holding tanks aboard the M.V. Tillikum and the M.V.

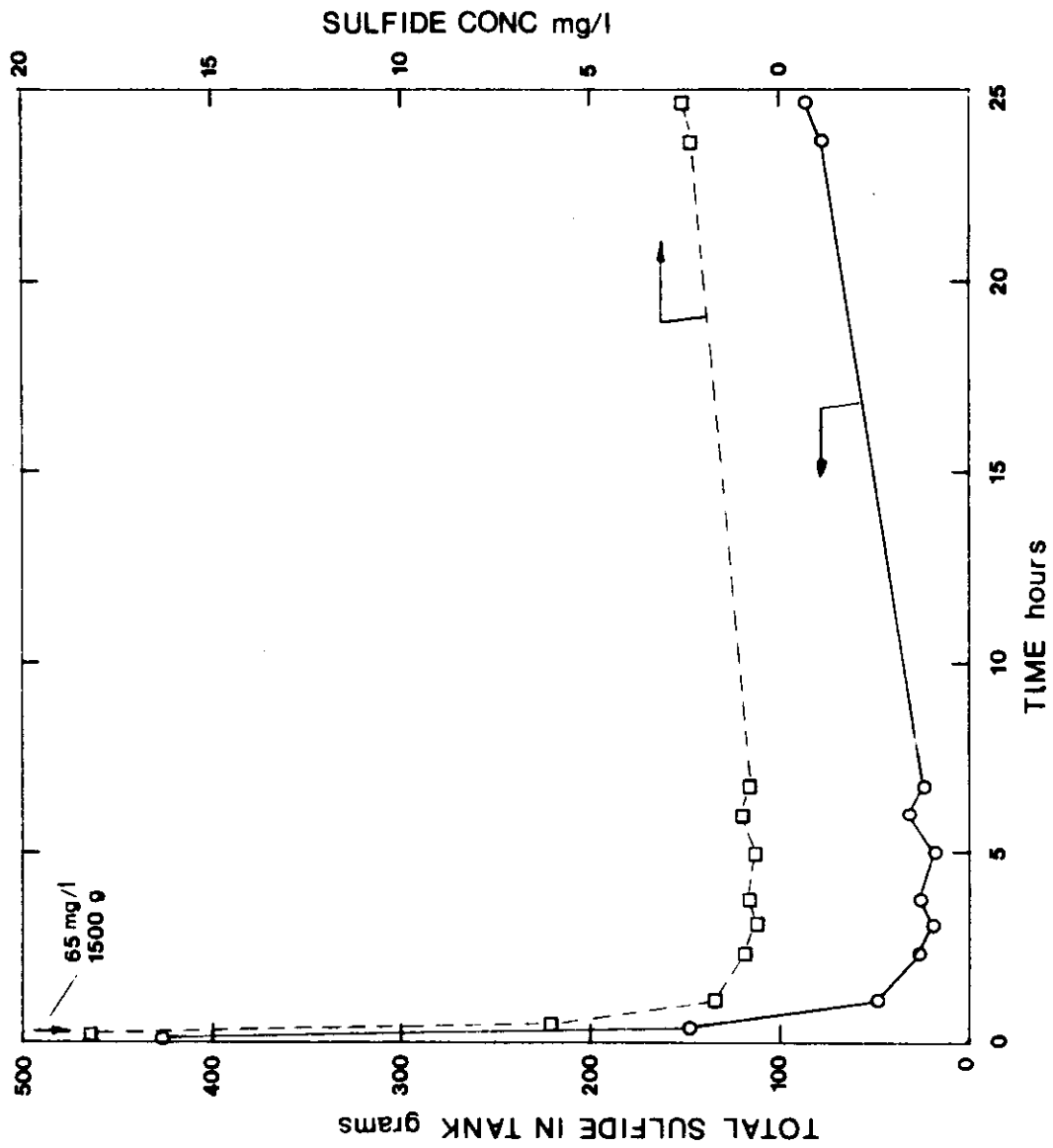


Figure 12 - Hydrogen peroxide addition to M.V. Tillikum holding tank, 9/22-23/76.

Klahowya. Doses were added at specified times by vessel crew members by flushing from passenger deck toilets which drain directly to the holding tanks. During the last two weeks of the sampling, hydrogen peroxide doses were added to the Klahowya holding tank through a funnel on the top of the holding tank.

Time periods for each of the observed conditions are shown in Figs. 13 and 14 for each vessel; and average sulfide concentrations are tabulated in Table 7.

1. E-Clor - One pint of the commercial odor control agent E-Clor (Pace Chemical Co.) was added daily.
2. No Chemical Addition
3. Hydrogen Peroxide (2 gallons/day) -- one gallon of 8% hydrogen peroxide was added twice daily in the early morning and evening.
4. Hydrogen peroxide (3 gallons/day) -- two gallons of 8% hydrogen peroxide were added in the morning, and one gallon was added in the evening.

Only one sample was taken from each vessel during E-Clor dosage. Both vessels had high sulfide concentrations, averaging over 3 mg/l sulfide. During the following period of no chemical addition, high sulfide levels were also found; particularly in the M.V. Tillikum holding tank.

The daily addition of two gallons of 8% hydrogen peroxide (about 600 grams H_2O_2 per day) from Jan. 22 to Feb. 1 resulted in a significant decrease in sulfide concentrations on both vessels. Morning hydrogen peroxide doses prior to sampling averaged about 50 mg/l during this period.

Dosing was stopped on February 2 and sulfide levels increased. While the concentrations remained relatively low (about 1 mg/l) on the Tillikum, levels on the Klahowya increased to about 2 mg/l. Average waste volume on the

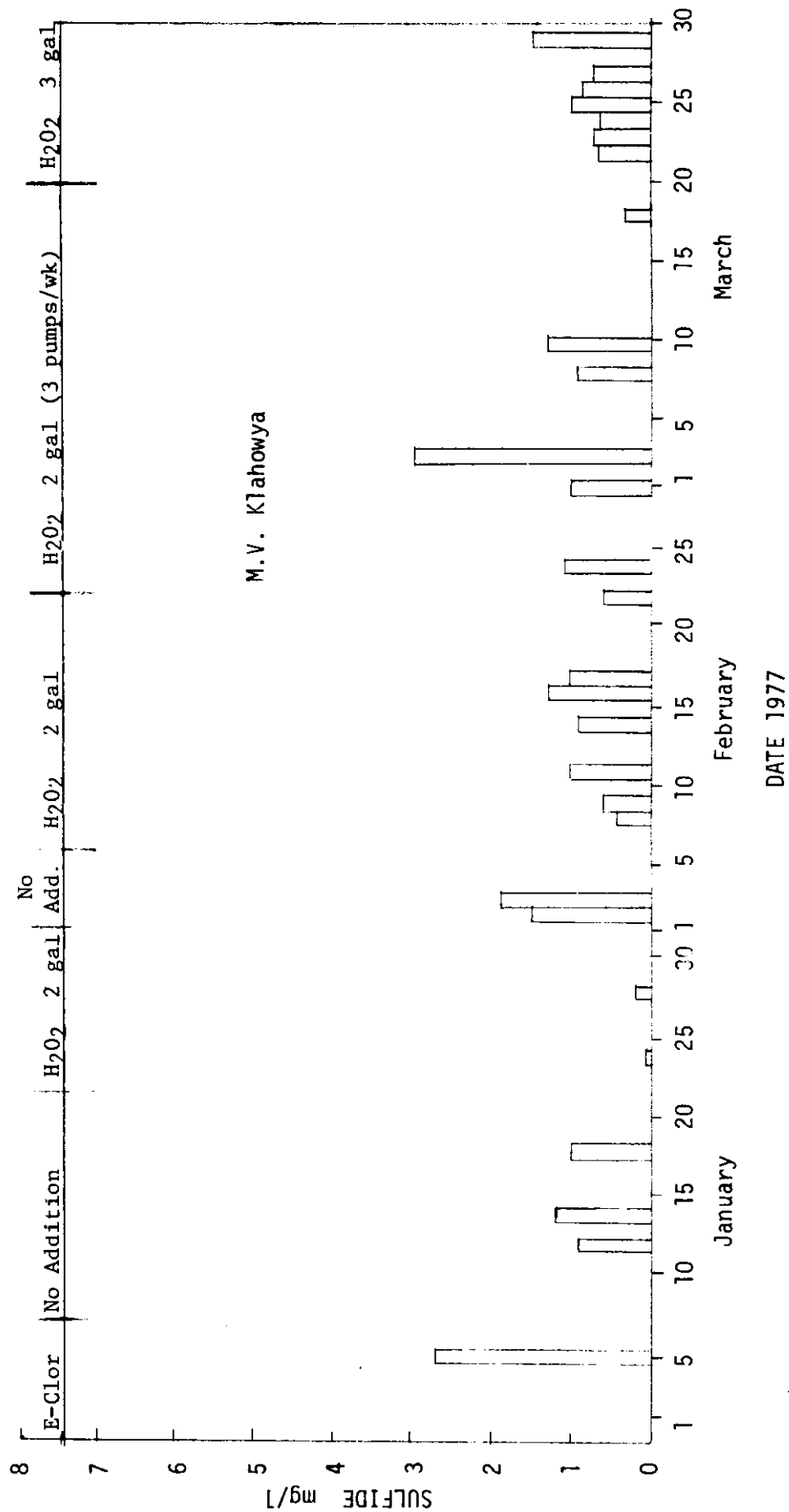


Figure 13. Sulfide levels in holding tank aboard M.V. Klahowya during monitoring study. Waste discharged nightly during first two months, then three times weekly for remaining period.

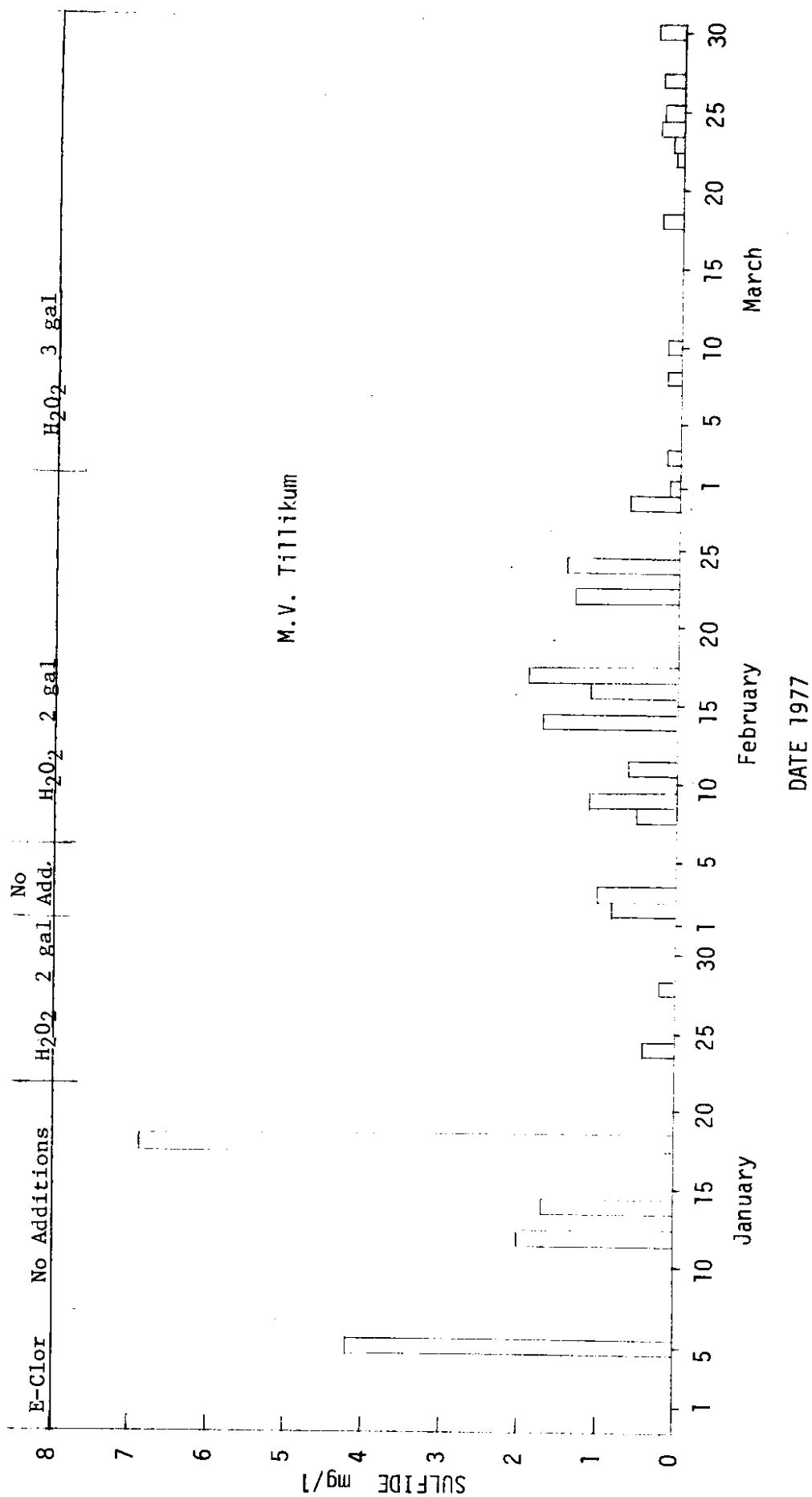


Figure 14. Sulfide levels in holding tank aboard M.V. Tillikum during monitoring study. Waste discharged three times weekly throughout period.

Table 7

Average Sulfide Concentrations During Monitoring Period at Various Dosings

	Tillikum	Klahowya	Ave. (both)	No. Samples
E-Clor	4.2 mg/l	2.7 mg/l	3.3 mg/l	2
No Addition	2.0	1.3	1.7	10
H ₂ O ₂ (2 gal)	1.0	0.7	0.8	22
H ₂ O ₂ (3 gal)	0.2	0.9	0.5	18

Klahowya was 1200 gallons. Aboard the Tillikum, waste volumes were higher, averaging over 4000 gallons at the time of sampling.

Following resumption of two gallons per day hydrogen peroxide dosing sulfide levels remained relatively high averaging near 1 mg/l on both vessels.

Finally, the 3 gallon per day dose (900 grams H_2O_2 per day) reduced sulfide concentrations to very low levels in the Tillikum holding tank. Sulfide concentrations were consistently below 0.5 mg/l.

In the Klahowya holding tank, high sulfide levels of nearly 1 mg/l occurred despite the increased dosage.

Following the two gallon morning doses, dissolved oxygen and sulfide concentration were monitored on three days for periods of 7-12 hours. Runs on several days led to two significant observations. On several instances vertical stratification of wastewater was observed with very little horizontal or vertical mixing. On these occasions, the peroxide dosage stayed localized in one area of the tank with much of the peroxide degrading to oxygen, which bubbled to the atmosphere. The effectiveness of the chemical dosage to most of the tank contents was greatly reduced. There is a need for mixing -- or at least stirring -- in the holding tanks.

On other occasions with better mixing, peroxide dosages in the Klahowya caused sludge solids to rise to the tank surface. Evidently, peroxide breakdown or organic matter oxidation caused bubbling which floated solids which had accumulated in the bottom of the tank. In the Tillikum, which has a sloped tank bottom and effective sludge removal, floating sludge was never observed. The poor location of bottom suction in the Klahowya tank resulted in sludge accumulations which used a significant

portion of the oxidant dosage.

It is unlikely that peroxide addition without some initial mixing and effective sludge removal will prove to be an effective, economical odor control method. Thus, the peroxide system design was modified to include these provisions.

System Design

Hydrogen peroxide is a clear solution that is completely miscible with water. It is available in concentrations of 35 and 50% weight. For costs estimates, a 50% solution is used, although dilution to 8% is currently required by the Coast Guard. 50% hydrogen peroxide is available in 15, 30, and 55 gallon containers at a price of \$.425 per pound in 15 gallon containers or \$.30 per pound in 55 gallon containers. Physical properties of 50% hydrogen peroxide are as follows:

Active Oxygen Content, % W	23.5
Lbs. per gallon at 20 C	10
Boiling Point °F	237
Freezing Point °F	-62

Industrial concentrations are inherently very stable and can be handled safely. The chemical itself will not burn, but its decomposition gives off oxygen and heat, which will support combustion. The rate at which gas is generated by normal decomposition is very slow, but it can increase through contamination with dirt, oils, rust, and metals such as copper, chromium, nickel, iron, manganese, and lead (FMC Corp.). Decomposition should not be

a problem if hydrogen peroxide is stored in its original container or in equipment of compatible material that has been thoroughly passivated. It should be adequately vented and stored in a dry, inside location. Safety goggles and rubber gloves should be worn when handling hydrogen peroxide because concentrated solutions have an irritating effect on the skin, mucous membrane, and eyes. It is recommended that a safety shower and eye-wash fountain be available to flush any spills.

The Department of Transportation classifies solution of H_2O_2 above 8% weight as "corrosive material," while the U. S. Coast Guard lists it as hazardous material in CFR part 146. It may prove necessary to use peroxide at this lower concentration. If so, safety showers and eye washes will not be required but still might be provided.

Chemical Addition and Mixing

Hydrogen peroxide will be added in slug dosages through existing plumbing fixtures on the passenger deck with a pumped recycle line to improve initial mixing. Cost estimates have been prepared and are described below.

Figure 15 shows a simplified flow diagram for hydrogen peroxide addition with mixing using a recycle line.

To provide good mixing of the holding tank contents, a recycle line is included in the estimate. Operation of the recycle pump will be controlled on a timed cycle estimated to involve two dosage periods per day, each lasting $\frac{1}{2}$ hour or less. Bottom suction to improve tank cleaning is also provided.

The recycle in this application is a direct connection from the pump discharge back to the holding tank. The pump will provide adequate energy input to stir the peroxide gradually into the entire tank contents. This system is

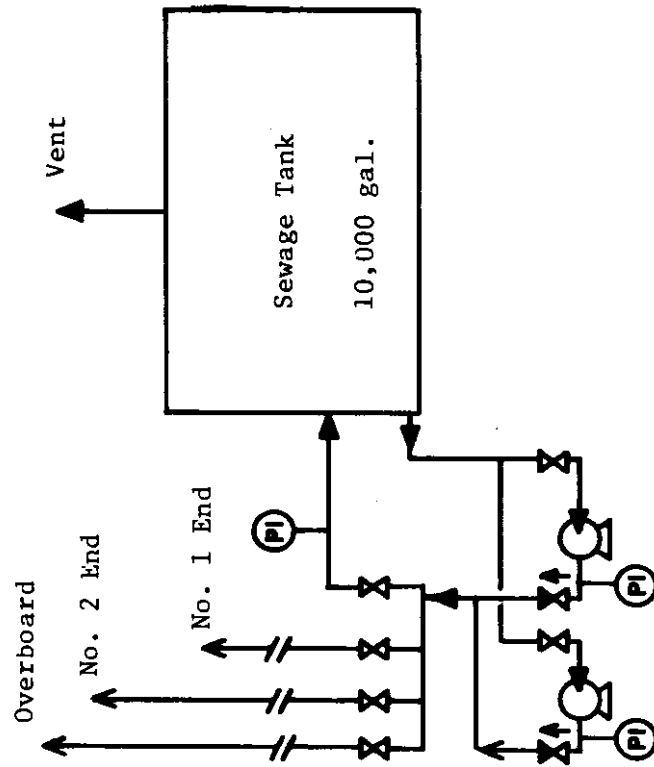


Figure 15: Simplified flow diagram for hydrogen peroxide, slug addition with recycle mixing.

simpler than that used for other chemicals or for the aeration system because a very low intensity mixing is adequate in this case.

Chemical Dosages and Costs

Bottle tests indicated that dosages of 40 to 60 mg/l peroxide were effective in inhibiting the generation of sulfide over a two day period. An on-board slug dose of 40 mg/l oxidizing a high concentration of sulfide, stopped sulfide generation for several hours, and reduced the subsequent rate of generation. A dose of 65 mg/l stopped generation for at least 7 hours. Dosages of 900 grams per day were effective in the Tillikum tanks, even when waste was more than a day old and the tank was more than half full.

It can be expected that inhibition would be longer once the tank is conditioned and low sulfide levels are present, since less peroxide will be utilized for sulfide oxidation and more will be available for bacterial inhibition. The added mixing provided by the recycle flow may also have the same effect by increasing the efficiency of sulfide oxidation. Operation of the recycle system for 15-20 minutes during each dosage would be desirable to disperse the dose through the tank and to reduce solids accumulation. The power costs for pump operation would be about \$136 annually. The total annual cost, including chemical and operation costs plus amortization of capital costs (8% interest, 20 year life) would be about \$1197 (Table 7).

Table 8. Cost Summary for Slug Addition of Hydrogen Peroxide with Recycle Mixing

Installation Cost

Recycle Line	\$2,676
Bottom Suction	<u>1,970</u>
Subtotal	4,646
Contingency 10%	<u>464</u>
TOTAL	\$5,110

Chemical Cost

3 gal. per day of 8% H_2O_2	
Equivalent to 0.5 gal. ² of	
50% H_2O_2	\$ <u>1.50/day</u>
	\$ 550 /year

Operating Cost

Sewage pump, 15HP, 1/3 hour 2times/day	\$ <u>.372/day</u>
	\$ 136. /year

TOTAL ANNUAL COST

including amortization at 8% for 10 yrs. \$1,197

C. Aeration

One of the simplest, inexpensive forms of oxidation is aeration using atmospheric oxygen. Aeration reduces the concentration of sulfides in several ways. Oxygen will react with sulfides to form sulfate. If dissolved oxygen is present in the wastewater, the anaerobic sulfate-reducing bacteria will be suppressed (EPA, 1974). The turbulence caused by aeration may also help to shear the filamentous bacterial slime from the tank walls. Chemical oxidation of sulfide by oxygen is relatively slow (Chen, 1974), but the microbially mediated conversion to thiosulfate or sulfate may be quite rapid. Minute or intermittent concentrations of oxygen will bring about a significant reduction in odor problem (Laughlin, 1964).

When oxygen is present in sewage, slime and sludge layers form an aerobic layer underlain by an anaerobic zone. Bacteria within the anaerobic layer will continue to produce sulfide which will diffuse outward. To prevent sulfide accumulation in the bulk liquid, oxygen concentrations of between 0.1 and 1.0 mg/l have been found to be sufficient to accomplish this control in flowing sewers (EPA, 1974).

Several means of introducing oxygen were considered including direct injection of air into the tank or injection into a pumped recycle line. The recycle systems were preferred because of inaccessibility of the diffusers in the direct injection system for inspection or maintenance, as well as doubts concerning their effectiveness in oxygen transfer.

The characteristics of the selected recycle aeration system are described in the following sections along with the results of studies that established the operating parameters for the design.

Air Injection into Recycle Line

Compressed air would be injected into the flow of sewage pumped by the existing sewage pumps through a new recycle line into the holding tank. Such a system is diagrammed in Figure 16.

A new four inch line will be provided entering the tank at the opposite end from the suction. Four, two-inch nozzles parallel to the bottom of the tank and equally spaced should be provided for good distribution and mixing. On those vessels having horizontal cylindrical tanks, the nozzles should be tangential to the bottom and spaced along the length. On vessels with two tanks, independent recycle piping should be constructed for each tank. A three inch fire water line will also be provided for flushing the new recycle line. A high pressure switch in the sewage tank will automatically shut off the fire water to prevent overpressuring the tank. Existing piping around the sewage pumps will have to be modified to facilitate installation of the recycle line.

A bottom suction nozzle must also be provided on some holding tanks to prevent sewage sludge from accumulating in the tanks. On many of the ferries the suction nozzle is 4-6 inches above the bottom of the tank, allowing an accumulation of solids. A small hopper should be provided so that it will be possible to drain the main body of the tank completely without drawing in air and losing suction at the sewage pump. The low level shutdown for the sewage pumps must be relocated to the new hopper. This change will still provide adequate net positive suction head for the pumps. There should not be any traps where solids could accumulate in the line to the pumps. With the suction nozzle at its new location, the suction line to the pump must be relocated lower. The control station for the pumps may also have to be relocated so that it is not obstructed by the piping. The existing fire water line

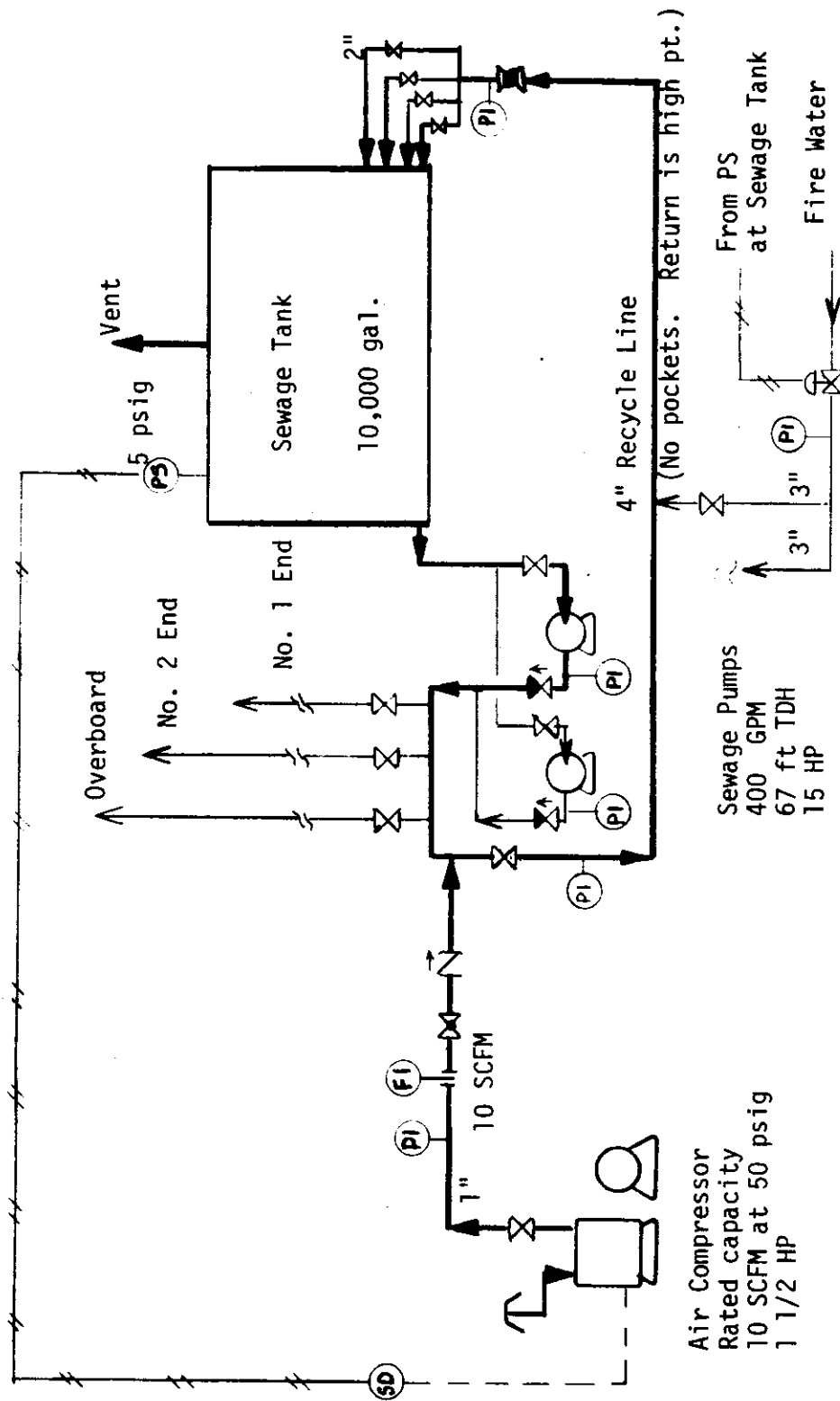


Figure 16. Simplified flow diagram aeration 10 SCFM to recycle line-new compressor

will be used to flush the suction which also must be extended to the new location.

The sewage pumps are rated at 400 gpm at 30 psig. Based on air rates used in successful odor control, 10 scfm of air or an air to liquid ratio of 2.5 scf/100 gallons was selected for design purposes (Dague, 1972; Laughlin, 1974; Pomeroy, 1969; and Sewell, 1975).

A small piston type compressor capable of supplying 10 scfm of air at pressures up to 50 psig is proposed. The compressor should be oil-less to prevent the introduction and buildup of oil in the circulating wastewater (Sewell, 1975). The new compressor would be located near the existing compressor and the sewage pump. A one-inch line will be provided for air injection. A flow indicator is needed in the air line to show the amount of air being added. A pressure switch will shut the compressor down in case of high pressure in the sewage tank.

The installation costs for the aeration system include \$5,395 for the recycle line, \$1,970 for the bottom suction, \$2,700 for the compressor piping, electrical work and instrumentation. With a 10% contingency allowance, the total installation is \$12,240 (Table 9).

The determination of operating parameters for the aeration system was based on laboratory measurements of wastewater oxygen uptake rates and on a mathematical simulation of the process.

Oxygen Uptake Studies

Oxygen uptake rate measurements were performed by measuring at various times the decrease in dissolved oxygen in an aerated sample. The rate of decrease was reasonably linear for time periods of 10 to 40 min. The rates were determined graphically as the slope of the oxygen decrease line at the middle of the time interval over which the decrease was measured. BOD values

Table 9. Cost Summary for Aeration

Air to Recycle Line Using a New Compressor

Installation Cost

Recycle line	\$ 5,945
Bottom suction	1,970
Piping	515
Instrumentation	1,420
Electrical	625
Compressor	<u>655</u>
Subtotal	\$11,130
Contingency	<u>1,110</u>
TOTAL	\$12,240

Operating Cost

Sewage pump 15HP	10m ea/hr	\$2.23/day	
		<u>.23</u>	
		\$2.46/day	\$ 896/yr.

Total Annual Cost

including amortization at 8% for 20 yrs. \$ 2,120/year

were also measured on samples taken periodically.

Figures 17 and 18 illustrate measured oxygen uptake rates (mg/l-hr) during prolonged aeration of wastewater samples at different temperatures. Generally, the results indicate an initial rapid rate of uptake as aeration is applied. This high rate rapidly decreases followed by an increase to a secondary maximum. Rates then decline again. Similar patterns of uptake rate changes in aged waste have previously been shown (EPA, 1974).

BOD₅ measurements taken during aeration are also shown in Figures 17 and 18. The results show a consistent decrease in BOD with time. The absence of large variations in the rate of BOD decline corresponding to variations in the oxygen uptake rate, indicates that oxygen uptake is not simply a function of BOD and may also be a function of other factors including inorganic reduced species present and the character of the microbial population. Close agreement was found between the decrease in BOD and the cumulative amount of oxygen taken up, showing good internal agreement of the test data.

The standard first order BOD formulation was used to describe the uptake of oxygen.

$$dL_t/dt = -dO_t/dt = -KL_t$$

in which L_t is the remaining ultimate BOD in the waste at time t , O_t is the oxygen concentration at time t , dO_t/dt is the instantaneous oxygen uptake rate, and K is the reaction rate coefficient, hr^{-1} .

Since 5-day BOD measurements were taken, the following correction was made to convert to ultimate BOD at time t :

$$L_t = \frac{y_{5,t}}{1 - e^{-120K}}$$

in which $y_{5,t}$ is the measured 5-day BOD present at time t . Rearranging and

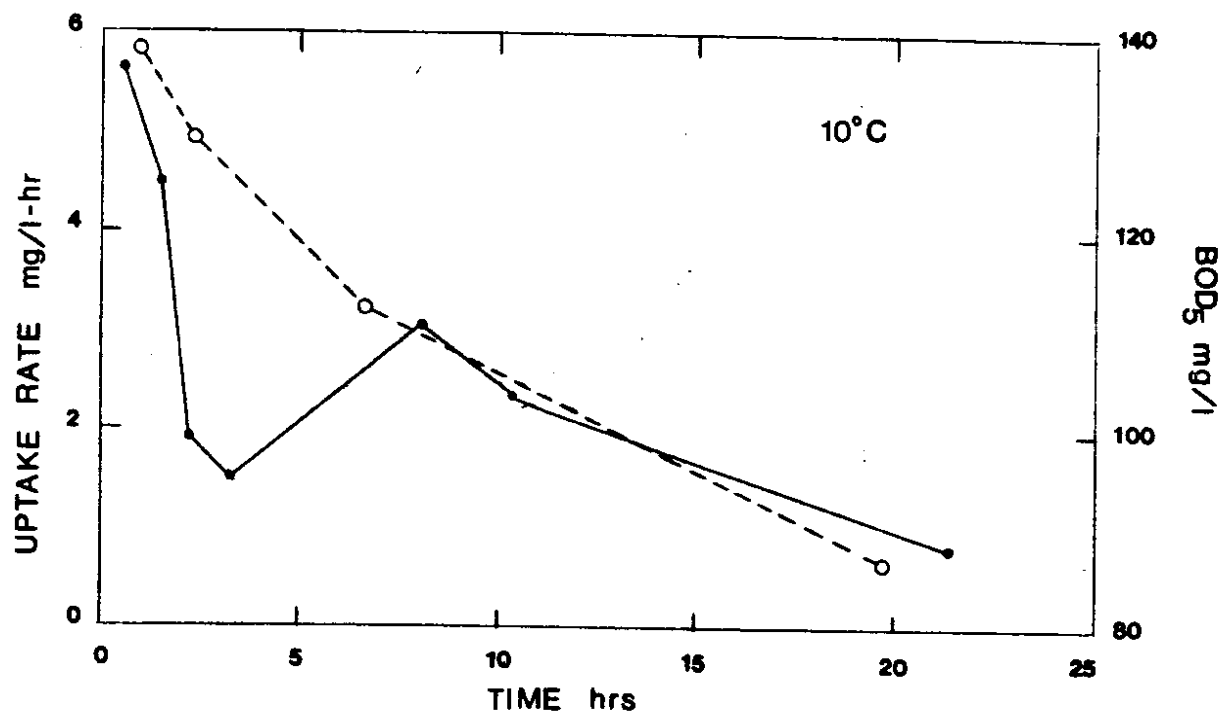


Figure 17 - Oxygen uptake and BOD changes with aeration time. Waste collected from M.V. Tillikum on 9/14/76. Solid line indicates uptake rate, dashed line indicates BOD values

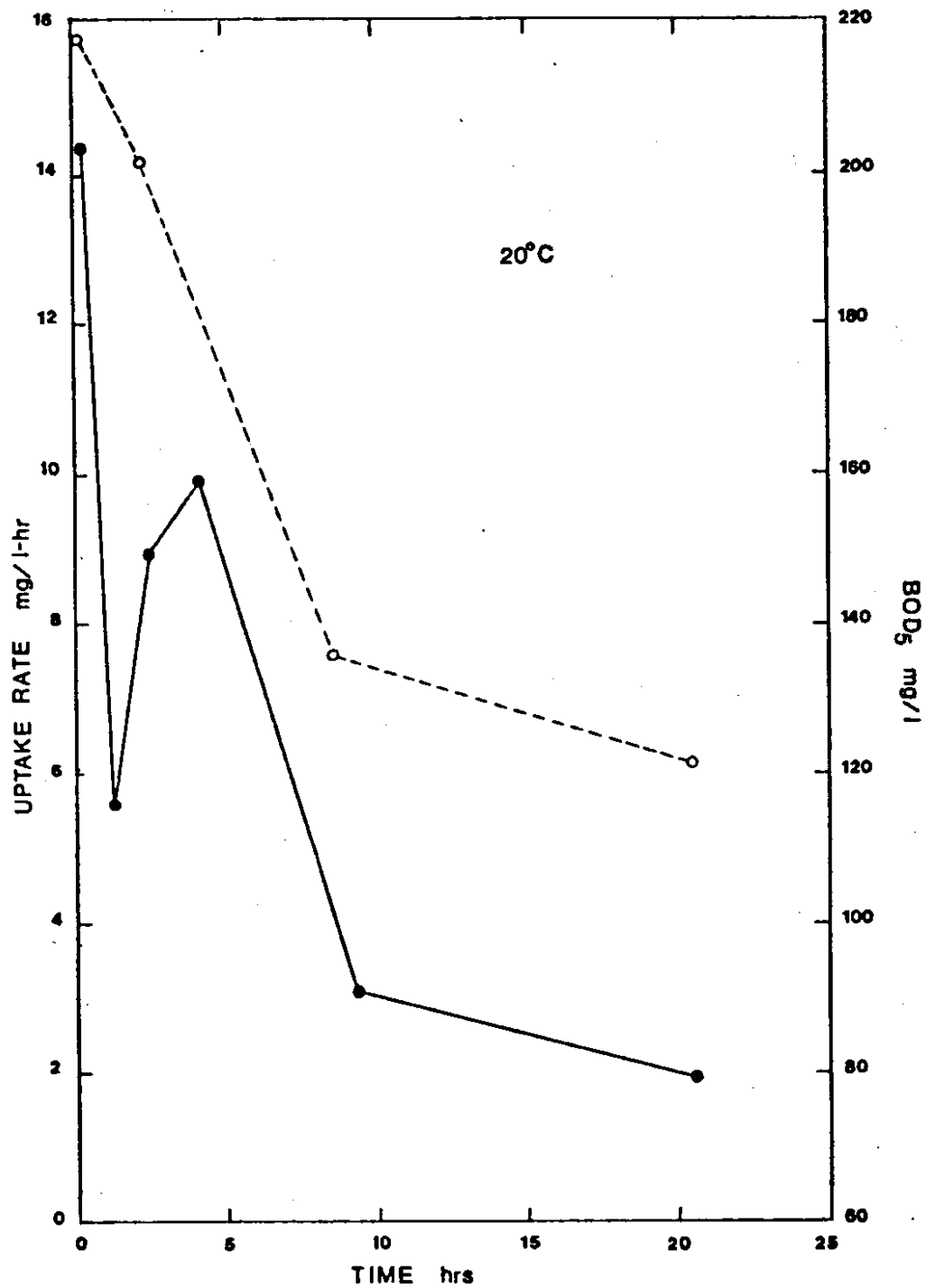


Figure 18 - Oxygen uptake and BOD changes with aeration time. Waste collected from M.V. Tillikum on 9/25/76. Solid line indicates uptake rate, dashed line indicates BOD values.

inserting the correction yields the following:

$$\frac{dO_t/dt}{y_{5,t}} = \frac{K}{1 - e^{-120K}}$$

The above equation was solved graphically for K at each point of measured uptake rate using interpolated values of $y_{5,t}$. K values were found to vary a great deal with time during the course of the aeration, generally following a pattern similar to the oxygen uptake rate.

K values throughout each experiment were averaged using a weighting factor equal to the length of the time period surrounding the measurement (Browne, Ferguson, Sylvester, 1976). Predicted oxygen uptake rates and BOD values, based on the initial BOD and averaged K values, are plotted for one wastewater sample in Figure 19. It can be seen that the predicted values for the two parameters vary significantly from the measured values, although over the one day period, the final values are nearly equal. The predicted oxygen uptake values are much more constant with time than the measured values.

To model more accurately the experimental uptake rate progression with time, a more complicated function could be used which would include the decrease of the K values. This may not be justified however, since the continuous inflow of raw waste and fresh BOD into the actual holding tank may result in nearly a steady state with respect to waste composition and overall uptake rate. Since the objective is to model the holding tank oxygen uptake, the use of a constant, averaged K value is probably a reasonable approximation to the conditions. The use of a more complicated function to fit accurately the experimental data did not seem merited. The sensitivity of the tank conditions to change in K values will be discussed subsequently.

The variation of K values with temperature is often described by the following formulation:

$$K_T = K_{20^\circ\text{C}} \theta^{T - 20}$$

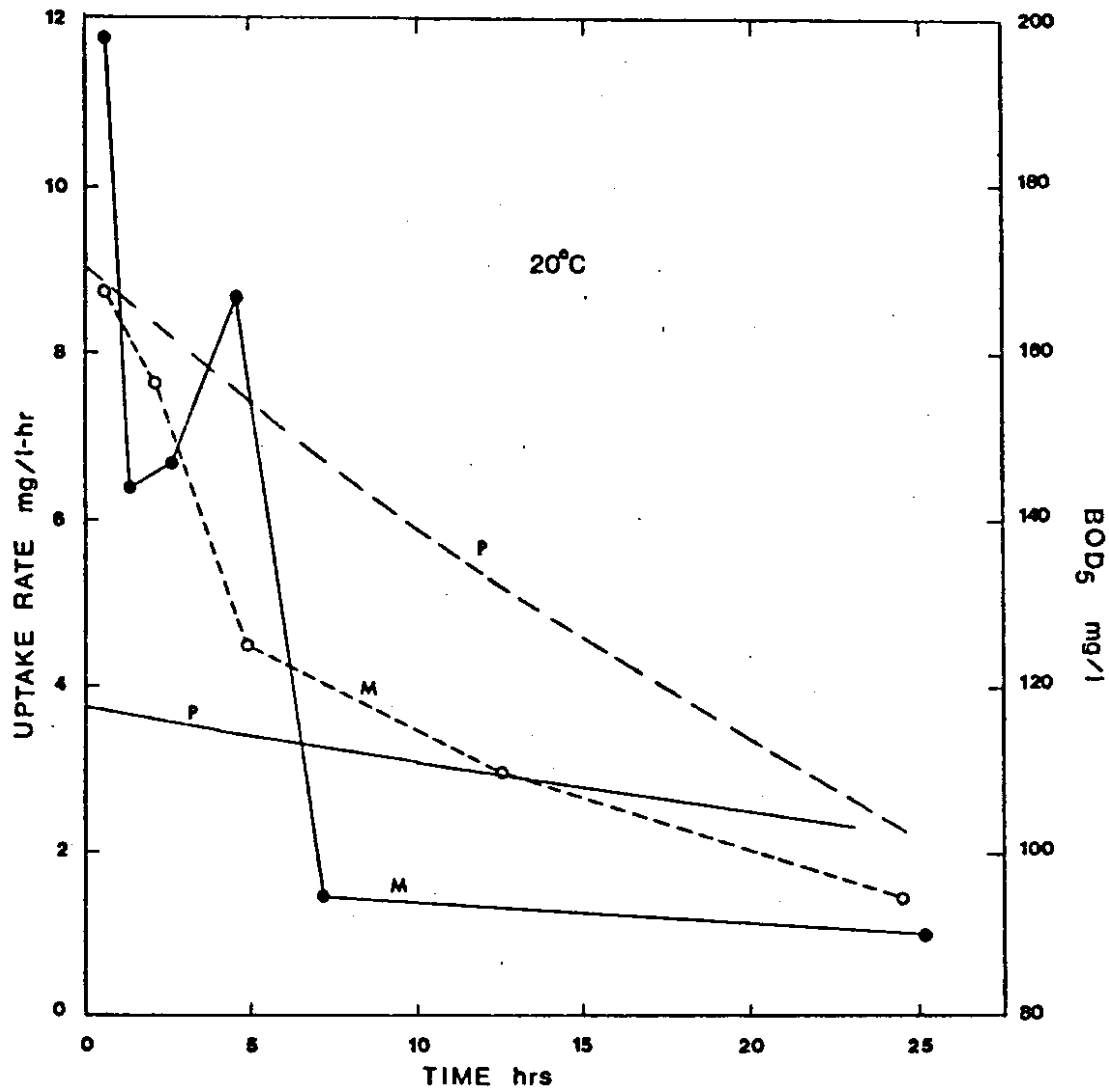


Figure 19 - Oxygen uptake and BOD changes with aeration time. Waste collected from M.V. Tillikum on 9/18/76. Solid lines indicate uptake rate, dashed lines indicates BOD values. P = predicted, M = measured.

where K_T is the reaction rate coefficient at temperature T and θ is an empirical constant. This equation can be linearized as follows:

$$K_T^{1/(T-20)} = \theta K_{20}^{1/(T-20)}$$

The above equation was plotted and a linear regression analysis run to determine the value for θ using an average value of K_{20} (0.024 hr^{-1}). The equation run below was found to predict accurately the experimental values except for the 10° C run.

$$K_T = 0.024 (1.172)^{T-20}$$

Aeration Model

To evaluate the significance of the above measurements in the holding tank system and to determine the aeration requirements, a simple mathematical model of the oxygen balance within the tank was constructed. Sources and sinks included in the models are listed below:

1. Biological oxygen uptake
2. Oxygen added with sewage inflow
3. Oxygen added by the recycle system

The formulations discussed below are presented in finite difference form as programmed for computer solution. Oxygen losses and gains (ΔO terms) are presented in terms of mass of oxygen added or removed from the tank during a time increment of Δt (hours). A constant rate of sewage inflow and constant inflow concentrations of dissolved oxygen and BOD are assumed. A time increment of 15 minutes was used throughout the runs.

Biological uptake of oxygen was formulated using the standard BOD model:

$$\Delta O_{\text{biol}} = -K_{T,t} L_t \Delta t V_{t+\Delta t}$$

where ΔO_{biol} is the mass of oxygen (mg) removed by biological uptake during time interval Δt , L_t is the BOD (mg/l) at the beginning of the time interval, K_T is the BOD coefficient at the waste temperature (hr^{-1}) and $V_{t+\Delta t}$ is the tank volume (liters) at the end of the time interval.

The BOD coefficient at temperature T was determined by the formula derived earlier

$$K_T = K_{20} (1.172)^{T-20}$$

where K_{20} is the value at 20°C.

The BOD at a given time was determined by the equation

$$L_{t+\Delta t} = \frac{(L_t - \Delta O_{\text{biol}})V_t + L_{\text{in}}Q_{\text{in}}\Delta t}{V_{t+\Delta t}}$$

where V_t is the volume at the beginning of the time interval and L_{in} and Q_{in} are the BOD and flowrate (liters/hour) of influent sewage.

Oxygen entering the tank with the sewage inflow was determined by the equation

$$\Delta O_{\text{inflow}} = C_{\text{in}}Q_{\text{in}}\Delta t$$

where ΔO_{inflow} is the mass of oxygen entering the tank (mg) with inflow during the time interval and C_{in} is the oxygen concentration in the inflow (mg/l).

Surface aeration was determined using the standard formulation which relates the flux of oxygen across a surface to the oxygen deficit present in the water and to a transfer coefficient.

$$\Delta O_{\text{SA}} = \frac{K_L A (C_s - C_t) \Delta t}{1,000}$$

where ΔO_{SA} is the mass of oxygen (mg) absorbed at the surface of area A (cm^2) during the time interval. C_S is the saturation concentration of oxygen, C_t is the oxygen concentration in the waste, and K_L is the oxygen transfer coefficient (cm/hr)

Weber (1972) gives the following expression for saturation concentration ($P_{O_2} = 0.21 \text{ atm.}$) for seawater dilutions of total dissolved solids, DS (grams/l) and T ($^{\circ}\text{C}$).

$$C_{s(\text{mg/l})} = \frac{475 - 2.65 (\text{DS})}{33.5 T}$$

The oxygen transfer coefficient was found using a formulation presented by Parkhurst and Pomeroy (1972) for sewer flows

$$K_L = 2(1 + 0.17 N_F^2) (\text{SU})^{0.375}$$

where U was assumed to be the average advective velocity due to recycle flow and S is the friction slope as determined by Manning's formula for open channel flow. N_F is the Froude number of the assumed flow.

The coefficient was reduced by 30% to account for the effects of salinity and surface active agents present in the sewage (Ogden, et al., 1959) and dimensional corrections were inserted to yield

$$K_L = 9.83 (1 + 0.17 N_F^2) (\text{SU})^{0.375}$$

This formulation yields a K_L value of 0.33 cm/hr when the tank is half full. Although this formulation is crude, this value is within the range of 0.2 and 0.6 cm/hr reported by several studies for stagnant water (Parkhurst and Pomeroy, 1972). It was hypothesized that surface aeration would play a relatively small part in the total oxygen balance in the tank and that an approximate solution would be sufficient.

Oxygen input from recycle aeration, ΔO_R , was included using the equation

$$\Delta O_R = C_R Q_R \Delta t$$

where Q_R is the recycle flowrate (1/hr) and C_R is the oxygen concentration in the recycle flow reentering the tank. The recycle concentration is assumed to be a constant factor multiplied by the saturation concentration adjusted to the recycle line pressure (Hay, 1956; Eckenfelder, 1966).

$$C_R = F_R C_s \left(\frac{P}{14.7} \right)$$

where P is the absolute pressure in the recycle line in psi and F_R is a constant factor which depends on the contact time and aeration system (Hay, 1956).

The overall mass of oxygen added or removed from the tank during the time period was then computed and divided by the volume at the end of the time interval to yield the oxygen concentration at the beginning of the next time interval.

$$C_{t+\Delta t} = \frac{O_{\text{initial}} - \Delta O_{\text{biol}} + \Delta O_{\text{inflow}} + \Delta O_{\text{SA}} + \Delta O_R}{V_{t+\Delta t}}$$

where O_{initial} is the mass of oxygen present in the tank at the beginning of the time interval. The new BOD value was then determined and the calculations were repeated for the following time steps.

Early runs with long aeration times showed the necessity to constrain the oxygen concentration to saturation concentration or less. Although supersaturation can occur in real systems, the high recycle volume and the length of the time increments yielded unreasonably high oxygen concentrations.

In real systems, supersaturation will be limited by the loss of oxygen through surface exchange by mechanisms which were not adequately included in this model. Although this effect was not quantitatively investigated, it was assumed that the error would be small.

For the initial "standard" run, the following parameter values were inserted.

Parameter	Value	Basis
K_{20}	0.024 hr^{-1}	measured average
T	17°C	measured average
L_{in}	168 mg/l	measured average
Q_{in}	552 l/hr	measured average (3500 gpd)
C_{in}	8 mg/l	seawater saturation
F_R	0.32	see discussion below
Q_R	90840 l/hr	pump capacity (400 gpm)
P	30 psig	pump discharge pressure
DS	25 g/l	90% seawater
Aeration Time	10 min/hr	see discussion below

This run was used as a base for the sensitivity studies discussed below. If not otherwise indicated, these parameters were used in all runs.

Figure 20 illustrates the results of the run using the above data with recycle aeration for 10 minutes each hour. Only the concentrations at the beginning and end of each aeration cycle are plotted since the decrease within the cycle was nearly linear. The results show that oxygen saturation is achieved following each aeration period for 12 hours of the filling cycle. The lowest oxygen concentration is slightly above 6 mg/l after 24 hours.

An overall BOD concentration reduction of about 20% from 168 to 136 mg/l occurs over the 24 hour period. This constitutes a significant reduction in the waste load eventually discharged to the sewerage system.

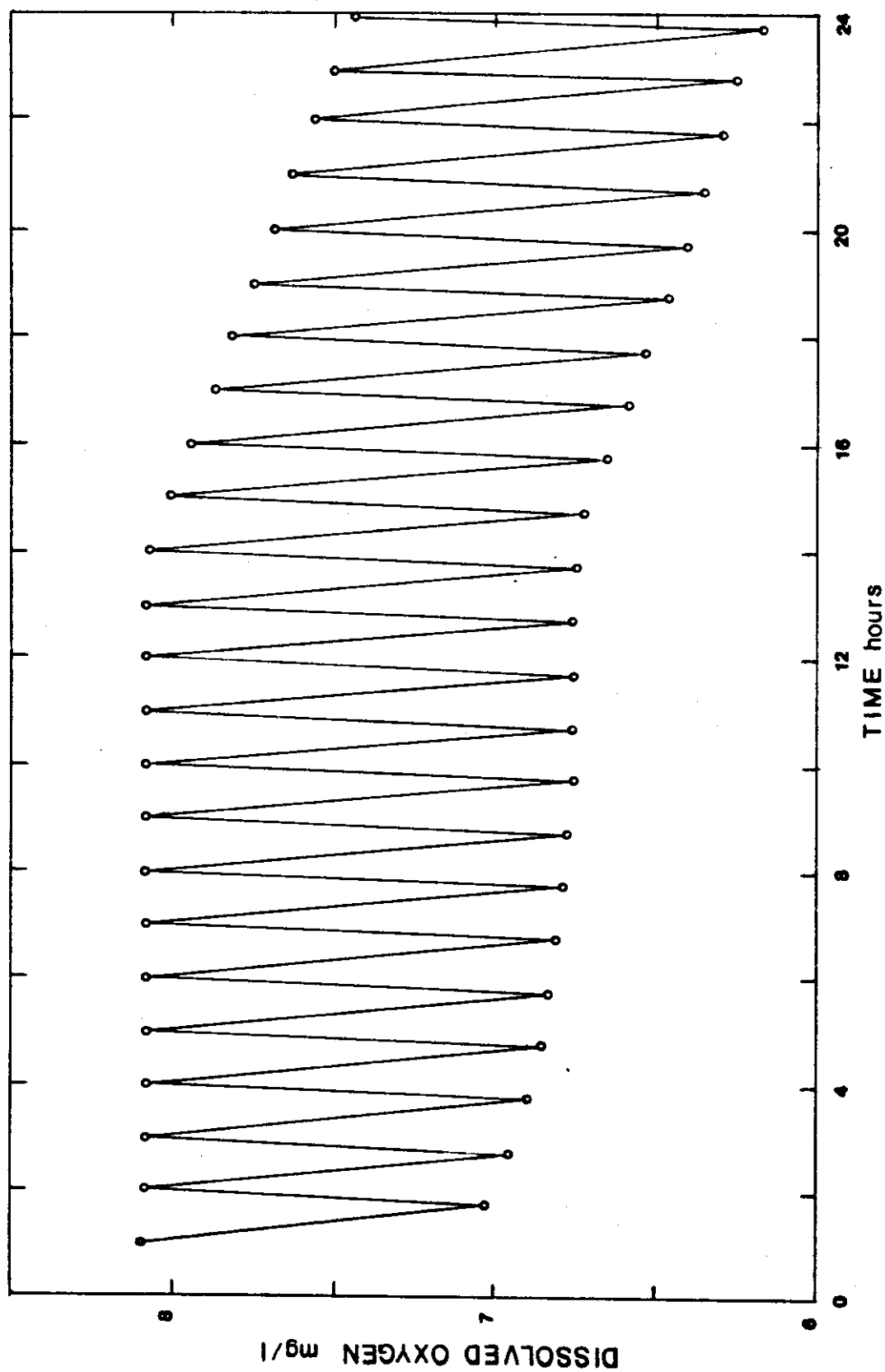


Figure 20 - Simulation results of dissolved oxygen concentration under standard conditions. Only values at the beginning and end of each aeration cycle are shown

Figure 21 illustrates the cumulative contribution of the three oxygen inputs to the total amount of oxygen added to the tank through the filling cycle. Total oxygen transferred averages 23.4 grams/hour or 33 mg/l based on the volume present at the end of the 24 hour cycle. The recycle aeration system provides by far the largest input of oxygen totaling 80% over the 24 hour period. The amount of oxygen supplied by the recycle system is limited early because the oxygen deficits are very small and by the constraint that the oxygen concentration in the tank cannot exceed saturation. As the tank volume increases, the mass of oxygen biologically taken up increases allowing the recycle system to provide increasingly greater mass with each aeration cycle.

The rate of oxygen entering the tank from the inflow is constant and this mechanism provided 19% of the total input over the 24 hour period.

Surface absorption of oxygen provides less than 2% of the oxygen with over half of this entering during the first two hours when the velocity across the tank due to recycling causes increased surface turbulence.

As discussed earlier, the maintenance of 1 mg/l dissolved oxygen is sufficient to prevent production of odors. Since the minimum oxygen concentration is the primary parameter of interest, it will be used to compare the effects of parameter changes to be discussed below. Complete depletion of oxygen must be avoided in the holding tanks, even though depletion for a few minutes per hour probably would not result in odor production. A considerable margin of safety should be provided in the operation cycle used on the ferries. The system must be failsafe since direct monitoring of dissolved oxygen or odors is not envisioned.

Figure 22 shows the effect of changing the length of aeration time each hour. Below 5 minutes of aeration per hour, the model indicates that the minimum dissolved oxygen reached in 24 hours drops rapidly and anoxic

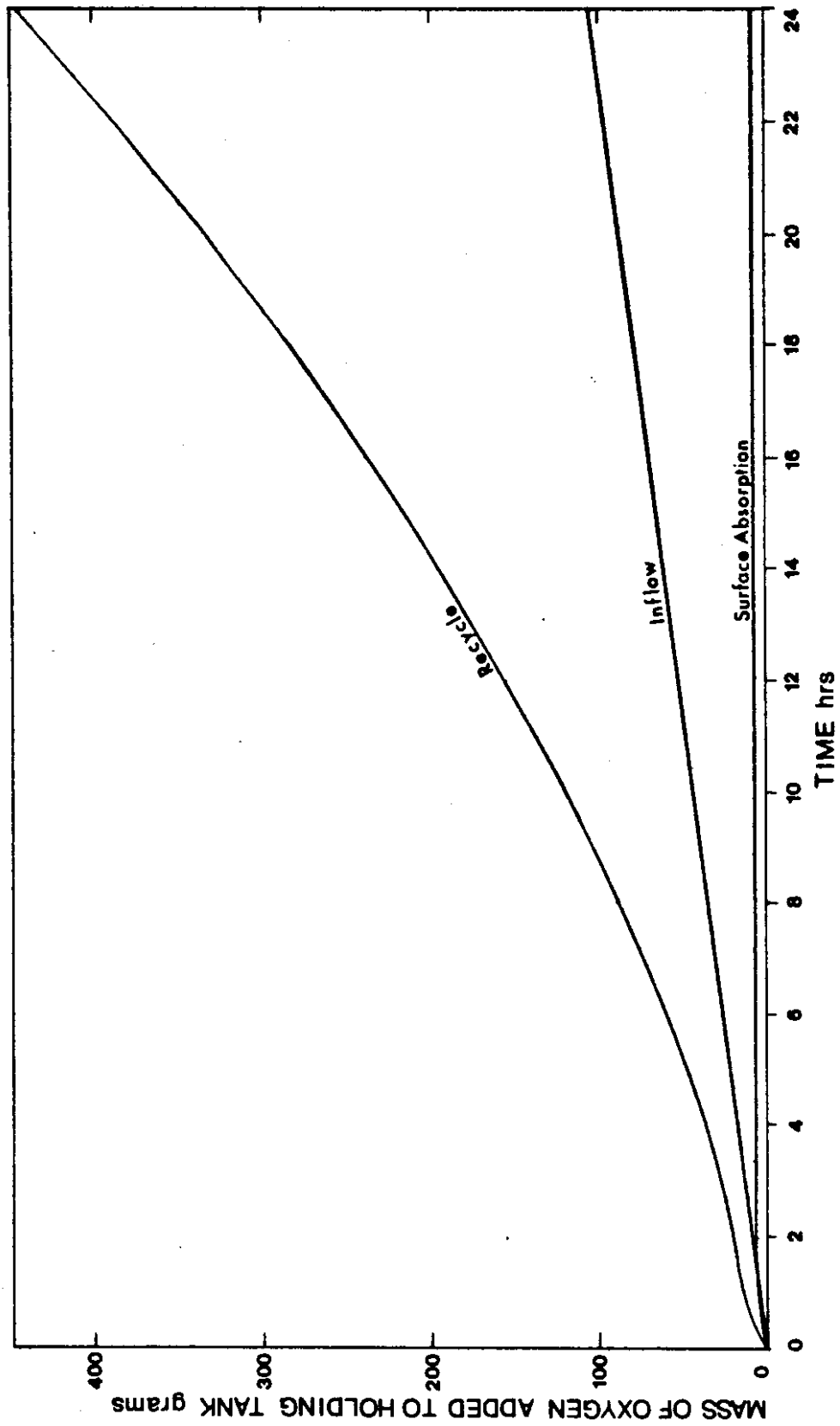


Figure 21 - Cumulative mass of oxygen added to holding tank during filling cycle under standard conditions by different mechanisms.

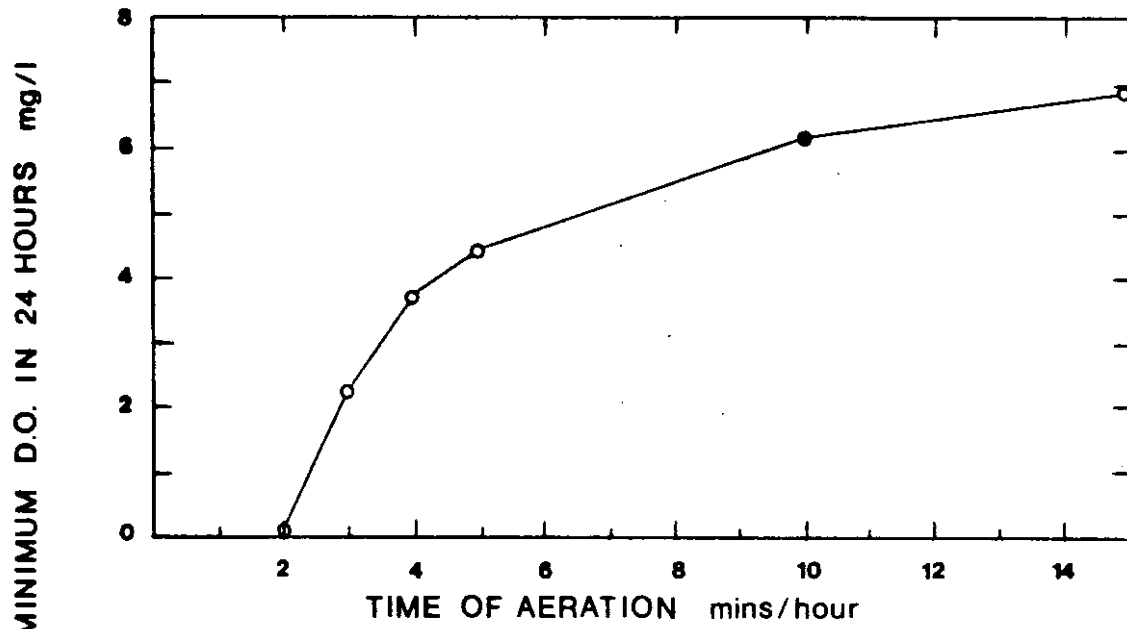


Figure 22 - Variation in minimum dissolved oxygen concentration with changes in the hourly time of aeration.

conditions were present with aeration less than 2 minutes per hour. Above 5 minutes per hour, the effect of increasing aeration time is decreased due to the inability of the waste to absorb oxygen above the saturation concentration.

It can be seen from these results that the aeration system can supply sufficient oxygen to the tank to prevent odor production with about 1/6 time operation or less.

The minimum dissolved oxygen concentration reached is very sensitive to F_R , the fraction of recycle line saturation reached in the recycle flow, as F_R drops below about 0.3. This value was initially chosen rather arbitrarily because it yields an oxygen concentration in the recycle flow equal to the saturation concentration at atmospheric pressure. Although this seemed to be a reasonable assumption, the results indicated that further refinement is necessary.

Hay (1956) investigated the solution of oxygen from injected air in an air flotation system with a baffled pressure retention tank included in the recycle system. He found F_R to be linearly related to the detention time as shown in the solid lines in Figure 23. With lower injection rates used than the 2.5 cf air/100 gallons recycle design used for the ferry tanks, Hay found that F_R values less than the assumed value of 0.3 are obtained even with a one minute retention time. In the proposed system, the detention time in the high pressure segment of the recycle line, between the point of air injection and the pressure control valve, is only about 5 seconds.

For a 5 second detention time, the pressure control valve must be located near the return to the tank. According to the qualitatively extrapolated line for 2.5 cf air/100 gallons recycle shown in Figure 23, this would yield an F_R value of about 0.25. It is believed that this value is a conservative estimate of the actual value which could be achieved due to the high degree

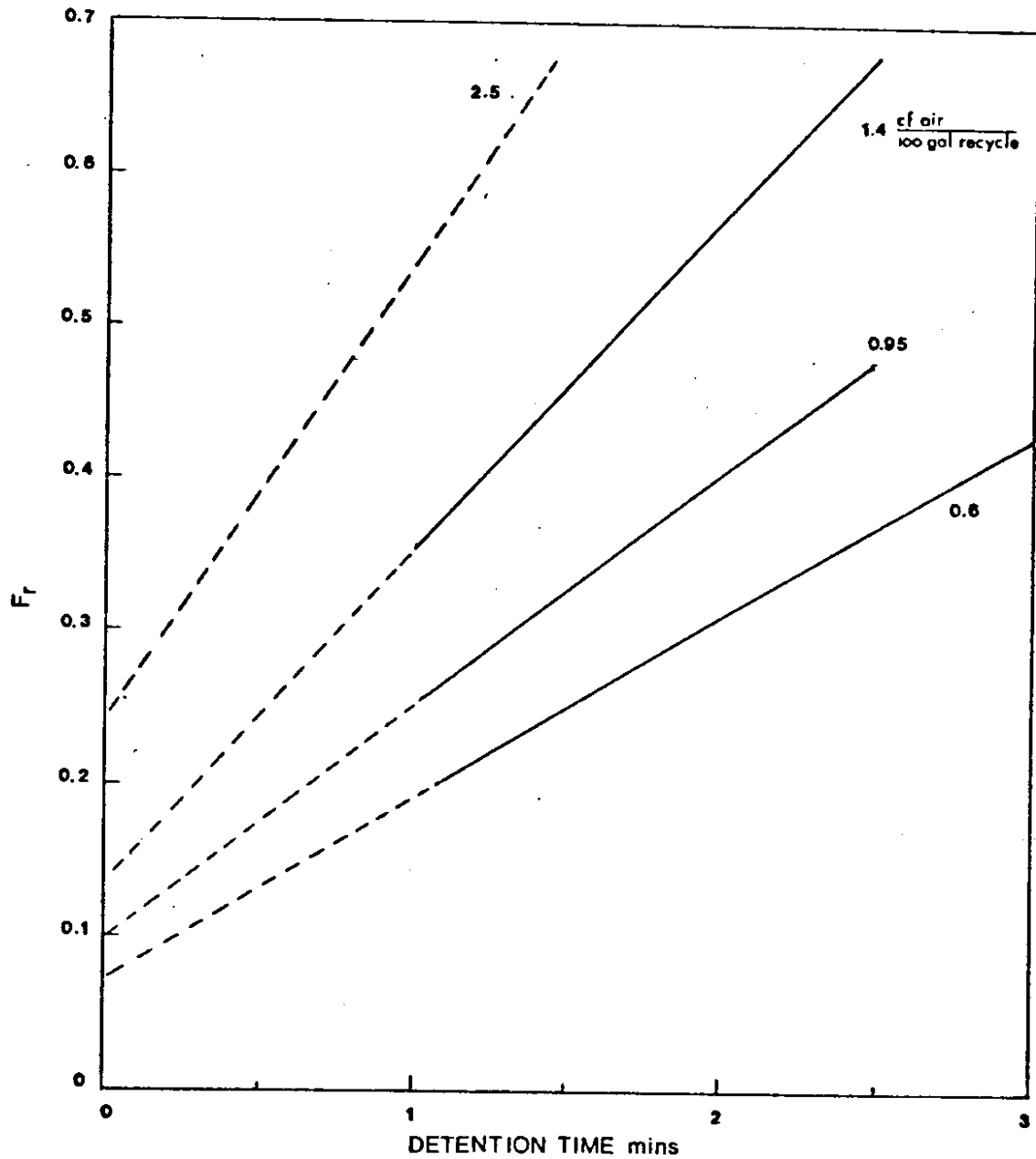


Figure 23 - Fraction of pressurized saturation concentration achieved in recycle line with detention time. Solid lines indicate the results of Hay (1956). Dashed lines are extrapolations.

of turbulence which will be present in the recycle line and the added dissolution of oxygen will occur as the excess air is released in the tank and bubbles up through the water.

Additional detention time could be achieved by the inclusion of a pressure retention tank in the recycle line following air injection. With a one minute detention time, a safe F_R value of 0.25 could be maintained with a smaller compressor delivering half the proposed air flow rate. The cost analysis for the proposed system indicated, however, that greater savings could be accomplished by reducing the aeration time since the power cost for the sewage pumps is ten times the power cost for the air compressor.

In other model simulations the effect of K_{20} and the waste temperature, itself, were found to be small for temperatures up to 20°C, which is one degree higher than the maximum found in a ferry holding tank. The rate of waste inflow was also varied over a wide range from 2,000 to 20,000 gpd with little effect on minimum oxygen concentrations reached in a filling cycle (10,000 gallon tank).

Finally, the oxygen concentration of the inflow, C_{in} , was chosen to be 8.0 mg/l which is approximately equal to the saturation concentration at 17°C. It was found that the system is almost completely insensitive to this parameter. It could be expected that the effect of C_{in} might increase with very high flowrates.

Operating Parameters and Costs

Based on laboratory studies and the results of the simulation models discussed in this chapter, recycle aeration can maintain sufficient oxygen in the holding tank to control production of sulfide with significantly less than full time operation. The injection of air at the rate of 10 scfm into a recycle line with a flow of 400 gpm maintained at 30 psig pressure for a period of 10 minutes per hour has been found to be adequate to maintain

aerobic conditions in the holding tanks for all anticipated situations based on the results of this analysis.

The operating costs for 10 min. per hour operation of the compressor and sewage pumps are estimated to be \$2.46 per day (\$896/year).

Although the model indicates that less than 10 minutes of aeration per hour will be sufficient, it must be emphasized that the preceding analysis was based on many assumptions. Some of the assumed parameters were shown to have little effect on the results. Some of the most important and sensitive parameters, most notably the efficiency of oxygen transfer in the recycle line, were based on extrapolated data. In these situations, an effort was made to apply conservative extrapolations.

To properly evaluate this system, a pilot study will be necessary to determine adequate aeration requirements under actual conditions. This study would involve installation of a recycle line and air injection system on at least one vessel and would best be carried out during the summer when the potential for sulfide production is highest due to warmer temperatures. Measurement of the two most basic parameters, the oxygen uptake rate and the efficiency of recycle oxygen transfer, could then be made by relatively simple, short term tests. After recycle operation for several days to acclimate the system to aerobic conditions, the system should be stopped and the decrease in dissolved oxygen monitored until the concentration reaches a low level (1-2 mg/l). Restarting the recycle system and monitoring the increase in dissolved oxygen in samples taken directly from the recycle line upstream of air injection and just before the return to the tank would further refine the results. Frequent sampling (1-2 samples per hour) during the test for BOD measurement would be necessary.

The test procedure should be repeated several times under varying conditions to obtain representative results.

The measured values for oxygen uptake rate and recycle oxygen transfer efficiency could then be used in a model similar to the one used in this study to arrive at aeration requirements for "worst case" conditions.

VI. EFFECTS AT TERMINALS AND RECEIVING SEWERAGE SYSTEMS

The wastewater pumped from holding tanks of the Washington State Ferries has potential impacts on the shore facilities receiving, transmitting, treating and discharging the waste. Certain effects have been identified at present; others are hypothesized at terminals where shore discharge is planned but not yet in service. All the effects are moderated by the methods of on-board odor control.

The factors which have been identified as having potentially adverse effects on shore facilities are: (1) the possible generation of sulfide in the force mains or sewers with low flows at or near the ferry terminals, (2) the ferry waste pumping rate relative to the hydraulic capacities of the receiving sewerage systems, and (3) the high salinity of the waste.

SULFIDE GENERATION IN FORCE MAINS

Sulfide will not be present in water leaving the ferries as a result of implementing one of the recommended alternatives and no odor problems are expected at the ferry terminals during pumpout. However, at several terminals there are force mains that may be stagnant long enough to cause sulfide generation as the stagnant waste water is displaced into the gravity sewers. The following discussions concern sulfide generation in force mains.

The occurrence of sulfide in sewers is an important factor in gravity sewer design where the maintenance of adequate velocities minimize sulfide generation. The discharge of hydrogen sulfide to sewers, however, can cause odors, corrosion, and hazardous conditions for maintenance crews in spite of good sewer design. The Municipality of Metropolitan Seattle (METRO) Council Resolution 2310, 3-01.03 and 3-01.04 strictly prohibits the discharge of hydrogen sulfide. Other wastewater agencies have similar regulations.

The slime layers can harbor sulfate reducing bacteria even though the sewage is fresh. Sufficient detention time in a full sewer or force main enables depletion of the DO; the depletion rate depends on the strength of the sewage (BOD) and the temperature. As found in the holding tanks, the sulfide production rate depends more on the wetted surface area than on the volume. Substantial sulfide can be expected in one hour detention in a full sewer, one-half hour for a small sewer (EPA, 1974): The smaller sewer has a larger surface-to-volume ratio.

Each of the terminals where wastewater pumpouts will occur was investigated for conditions leading to generation of sulfides in force mains. At present, force mains at Edmonds and Fauntleroy terminals may have sulfide generation. The volume of stagnant sewage in the force mains could not be

estimated precisely, but is about 1,000 gallons at each terminal.

Design at Anacortes and Mukilteo should be made to avoid stagnant force mains if at all feasible. At these installations it may be possible to slope the pipes to enable complete drainage to the manhole and back to the ferry holding tank.

Corrective measures at Edmonds and Fauntleroy must either inhibit sulfide generation or remove the sulfide. Chemical injection and force main aeration were judged to be too complex or costly to use. Force main flushing, using either fresh or salt water, was selected as a feasible method of controlling sulfide generation in the stagnant force main.

Flushing the force main with unpolluted water would inhibit sulfide production due to the high DO and remove organic nutrients for sulfate reducing bacteria.

Fresh water flushing would require an air break to prevent back suction and pollution of the fresh-water supply. An elevated water storage tank on the trestle or special plumbing similar to that for toilet flushing with high volume capabilities would be adequate. 1,000 gallons of flushing water at 250 gpm injected after the last ferry holding tank pumpout each day should be sufficient to displace the wastewater in the entire force main. Based on Seattle water rates ($14.2 \text{ ¢}/100 \text{ ft}^3$) this would cost about \$70 per year over the additional sewer cost which would be \$230 per year ($47 \text{ ¢}/100 \text{ ft}^3$). Installation costs have not been estimated.

Salt water flushing could be accomplished either with a pump from the dock or with the fire water from the ferry. A shore pump could be started manually after the last pumpout with a timing switch to terminate the cycle after the required volume has passed through. This pump would be of sufficient capacity to insure good flushing in a relatively short time.

A tank flushing system could be used with a lower capacity pump. Operating and installation costs for a shore pump system have not been estimated.

The preferred alternative, subject to layover constraints, is to have the ferry just prior to the longest stagnant period of the day flush the force main. The ferries are presently adequately equipped to perform this function. The length of time required for pumping would depend on the capacity of the particular ferry's pumps with the appropriate duration calibrated for the passage of approximately 1,000 gallons. Some vessels have the capability of injecting fire water (seawater) at the suction side of the sewage discharge pumps. In such cases, the pumpout rate is greater than 250 gpm and a flushout time of 5 minutes would be sufficient at Fauntleroy and Edmonds

Based on tests of flushing conducted at the Fauntleroy terminal, it is recommended that force main flushing be performed once each day:

1. At the end of tank pumpout, which should include two brief cycles of internal washing using the cellar nozzles, the sewage pumps will be shut off by the low level control. The valve between the holding tank and the pump suction should be closed.
2. The connection to fire water should be opened.
3. The sewage pumps should be restarted and operated for 5 minutes, then fire water and sewage pumps should be shut off.
4. The valve in Step 1 should be reopened.
5. On the car deck, the valves should be changed for 30 seconds of fire water flushing of the trestle hose and piping.
6. At the end of the flushing of connections, the line should be drained back to the holding tank.

7. All valves should be returned to the positions used during the wastewater collection cycle.

The procedure outlined above can be used on the Evergreen State class vessels with no changes in piping or valving. The increase in the complexity of the pumping procedure is minimal and can be accommodated by the engine room crew. The increase in pump-out time is 3-5 minutes, since the 5 minute pump flushing and 1/2 minute connection flushing replace the 3 minute connection flushing time now used. The 5 minute flushing time is quite critical and is predicated on a line volume of 1200 gallons (1000 in dock lines and 200 gallons in the vessel lines) and a 350 gpm pump rate. at least 20% excess flushing water should be used to reduce BOD and SS in the force main in order to avoid oxygen depletion in the stagnant period. The costs of flushing are approximately \$300/year in additional sewage charges at each terminal, and minimal costs of operating pumps on one vessel for 3-5 minutes each day.

EFFECTS OF SALINITY ON SEWAGE TREATMENT PLANTS

The sanitary engineering literature was reviewed to assess the maximum continuous or shock loads of salt that could be accepted by various treatment processes without impairing their effectiveness. The processes considered were sedimentation, trickling filtration, activated sludge, and anaerobic sludge digestion. No criteria could be ascertained for effects of a saline shock load on sedimentation, but the following criteria were derived for the three biological processes.

TABLE 10 CRITERIA FOR TOLERABLE SALINITY DOSAGES*

	Maximum Tolerable Shock Load	Maximum Tolerable Steady State Concentration
Anaerobic Digestion	29	43
Activated Sludge	29	100
Trickling Filters	36	100+

* as % seawater, 100% = 28,000 mg/liter NaCl

The tabulated salt levels are those, as indicated by the literature, at which adverse effects were first noted or below which process efficiencies would not be impaired.

Analytical models were developed using these salt level criteria, flow data, and certain plant parameters for several important unit process configurations to indicate the highest relative ferry waste loadings that can be accepted by a particular treatment plant (Lellelid, 1977).

The models (Lellelid, 1977) have been used to determine the smallest size sewage treatment plant, based on average flow rate, which could accept ferry waste discharge from the Washington State Ferries. This analysis will be based on the maximum salt loading criteria, though hydraulic factors may be the more limiting constraints in some situations.

Each of the major biological treatment processes was investigated, and recommendations made to preclude any impacts at the lower flow rates.

The Nature of the Ferry Waste Stream: Pumping rates (q) of the vessels range from 75 to about 500 gpm with most being between 200 and 400 gpm. Discharge volumes (v) approach 10,000 gallons per pumping schedule as a maximum. The only constituent of concern in this waste is the NaCl due to the use of seawater flushing; the average salt level (f) is equivalent to 85% standard seawater.

Anaerobic Digestion: Dilution of the waste will be required if

$$Q/v \leq f/C_{\max} - 1$$

in which Q is the average daily plant flow rate and v is the average daily volume pumped from the ferries, and the relevant level of $C_{\max}$ is found in Table 10; the discharge rate is unimportant.

$$Q/v = (85/43-1) = 1$$

The implication is that the ferry waste volumes generated must be equal to or less than the freshwater sewage streams.

A case in point is the future Anacortes plant which will have an initial average flow of 2-3 MGD. The four or five ferries may generate up to 50,000 gallons per day into this system: in this case the safety factor is 40 to 60 times. Seawater from ferry wastes will have no ill effects on this process at any of the receiving sewerage systems.

Trickling Filtration: This unit is preceded by a sedimentation basin: assume the basin is a CRF (circular radial flow reactor) with a minimum detention time (θ) of one hour at the average plant flow rate (Q).

This will afford the worst case C_m , where C_m is the maximum concentration in the trickling filter.

For $q = 400$ gpm, the pumping duration is

$$t' = v/q = 10,000 \text{ gal}/400 \text{ gpm} = 25 \text{ min.}$$

and

$$t'/\theta = 25/60 = 0.42$$

This value, used in the model presented graphically in Lellelid (1977), results in

$$C_m/C_o = f(0.42) = 0.39$$

$$C_o = \frac{49}{Q-0.24}$$

C_o is a derived concentration parameter related to the diluted salt concentration in the plant inflow, and in this case, solving the two equations yields $Q \geq 0.77$ MGD, the value needed to assure no effect of the salt discharge.

The value of Q is relatively insensitive to variations in q between 200 and 600 gpm for the fixed volumetric flow of 10,000 gallons. An 0.8 MGD plant is very small; the sedimentation basin has a volume of only 33,000 gallons at this value of Q and θ . This short duration slug input would displace 10% of the volume causing a hydraulic upset in the basin. Certainly lower pumpout rates or flow detention would be prescribed; this would, in turn, decrease C_o well below the constraining level at the given flow rate.

Activated Sludge: The case of the biological reactor (CMR) receiving raw waste directly without primary sedimentation, represents the worst case situation. Only if impacts are severe will the case for a CMR preceded by a sedimentation basin warrant investigation.

Recycle may be employed at the plant but is ignored in the analysis, and θ is based on the average plant flow rate and the reactor volume.

The lower limit of $\theta = 3$ hr. is chosen to assess the highest values of C_m in the reactor. Generally, longer detention times of 6-24 hours are used in small activated sludge plants.

$C_{\max}$ is 29% seawater (Table 10) for shock loads to the activated sludge system. The effective input level in this case is:

$$C_o = \frac{f}{Q - \frac{10,000}{\theta}} = \frac{1.22 (10^{-3})q}{Q - 0.08}$$

As before, values of q ranging from 100 to 600 gpm are tested to find the respective minimum levels of fresh water waste necessary for proper dilution of the salty waste at this pumping rate and volume. It is found that Q is not very sensitive to the rate of salty waste flows in this range, and Q must be greater than 0.2 MGD (140 gpm) to have an appreciable salt effect on the microbes in this process. All activated sludge plants expected to receive ferry wastewater are considerably larger than 0.2 thus no salt toxicity is expected in this process.

Obviously if the plant was less than 0.2 the applied flow rates would be too high for the small system; the high flows would be detained and the salty inputs would be made over a longer time frame. This would lower the C_o , and hence the C_m , seen in the reactor; and at the same time, the biology could become acclimated to the relatively constant input levels of salt -- the shock loading criterion would no longer apply.

The results of all analysis are that no biological problems from salinity are expected at any plants receiving ferry waste water.

HYDRAULIC CONSIDERATIONS

The rate at which the ferry holding tanks are discharged varies with the class--ranging from 700 gal. at 75 gpm to 16,000 gal. at 800 gpm.

It is of interest to assess the ability of the receiving sewerage system to contain adequately the peak discharge rates associated with each terminal facility. Due to the singularity of the topography and configuration of the collecting sewerage at each facility the evaluation was made on an individual basis for each facility.

Only at the Seattle terminal were possible problems with the hydraulic capacity of the sewers found. The configuration of the terminal piping and of the receiving sewers are such that a 365' long, 12" diameter sewer along Alaskan Way has a slope of 0.0020 and a full flowing capacity of 715 gpm, which suggests potential difficulties if two vessels were to pump simultaneously. The MV Walla Walla claims a total pump capacity of 1,000 gpm (2 pumps @ 500 gpm), but noted a flow rate of only 386 gpm with one pump. With both tanks being emptied together, friction losses would be greater since head loss is proportional to the square of the flow rates. A quantitative figure for expected discharge rate is not possible without knowing the pump dynamics. Yet both pumps together were not likely to be discharging at a rate higher than 750 gpm. This rate is at the limit of the sewer capacity, the simultaneous discharge of 2 ferries could not be conveyed by the sewer. Discharge from two ferries should be avoided at the risk of backing up the sewers and overflowing onto the street at the terminal entrance.

No other significant operating problems are foreseen at any of the ferry terminals or in any of the sewerage systems presently receiving ferry waste-

water; however, neither the sewage system at Mukilteo (Gray and Osborne, Inc., 1975) nor the treatment plant can accept a 400 gpm discharge rate -- ferry waste detention is recommended.

VII. Implementation

The existing wastewater handling and holding system was found to be effective and practical. The modifications to control odors during holding and discharge should be implemented in three stages, the first two of which are already partially completed.

The first stage, which has been implemented, is abandoning the use of E-Clor, an ortho-dichlorobenzene based product. The chemical was found to be poorly effective, possessing potential health hazards, detrimental effects treatment plants and receiving waters. Use of the chemical was stopped early in 1977.

The second stage, which is partially implemented, is the use of H_2O_2 in slug doses, added through urinals or other existing plumbing. This alternative (using 3 gallons per day of 8% H_2O_2) is moderate in cost and has been shown to be quite effective, suppressing sulfide to about 0.5 mg/l in the holding tanks. To make this procedure fully effective, recycle mixing capability and bottom suction must be included in each holding tank. The modifications, which are described in the report, are moderate in complexity and cost.

The third stage to aeration by injection into a recycle line is considered to be most effective, reliable, and easy and safe to operate of all alternatives investigated. A prototype system, including installation of a recycle line, compressor, valving, indicators and other instrumentation and bottom suction, is recommended in order to carry out pilot studies to optimize the design and operation of the system. The preliminary design and costs in this report can readily be used for such an installation. They could be used for installation on all vessels, but much is to be gained by studying operation and refining the design.

Force mains, which remain filled during stagnant periods between pump-outs, exist at Fauntleroy and Edmonds. At these locations a flushing procedure, described in the report, should be used each day. The flushing should remove wastewater and avoid sulfide release in sewerage systems during pumpout.

Liaison with sewerage agencies and their consulting engineers at locales with ferry wastewater discharge should be strengthened. Long, undrained force mains should be eliminated in the design stage, and pump stations must be carefully designed to handle the short duration, high flow rate pumpouts economically and without odor generation and release.

Appendix 1. Conversion to Overboard Discharge

One option that was considered and abandoned early in the study was conversion from a holding and on-shore discharge system back to a direct overboard discharge system. Early in the study the Environmental Protection Agency promulgated regulations for overboard discharge and marine sanitation devices (Federal Register, 1976), which modified the earlier proposed Marine Sanitation Device Standard of the Coast Guard (Federal Register, 1975).

Two types of flow-through devices are allowed on existing vessels. A "Type I Marine Sanitation Device" permits a fecal coliform bacteria count not greater than 1,000 per 100 milliliters and no visible floating solids in the effluent. No visible floating solids is defined as 10% or less of the total suspended solids retained on U. S. Sieve No. 12 (Federal Register, 1975). Type I devices provide no treatment of the waste discharged except that fecal coliform bacteria, which are not well suited for cold salt water environment, are killed. A "Type II Marine Sanitation Device" is one which produces an effluent having a fecal coliform bacteria count not over 200 per 100 milliliters and suspended solids not greater than 150 mg/l. The waste treatment that these devices provide is a moderate level of suspended solids removal. The only flow-through device allowed on existing vessels after January 30, 1980, is Type II unless the vessel is equipped with a USCG certified Type I Device installed prior to January 30, 1978, which may then be used for its operable life (Federal Register, 1976). Type I Devices may be installed after January, 1978, but must be replaced by January, 1980.

Several considerations are involved in a decision to return to overboard discharge. First, installation of a certified flow-through sanitation device does not insure that overboard discharge of sewage will be permitted. States may prohibit the discharge of sewage, treated or not, if the EPA has determined "that adequate facilities for the safe and sanitary removal and treatment of

sewage from all vessels are reasonably available" (Federal Register, 1975). Washington State does not allow the discharge of organic or inorganic material which may cause pollution of the waterways (RCW 90.48).

Second, Type I devices would have to be installed prior to January 30, 1978 in order to be used after January 30, 1980 - a time schedule that presents severe problems for back fitting the 18 ferries in the system. The devices, however, are not complex and commonly would involve only chlorination and maceration. Preliminary designs and cost estimates for devices to meet the standard were prepared (Parrish, Ferguson and Sylvester, 1976) The results showed little if any cost advantage compared to holding and on-shore discharge with an odor control method. There is no economic incentive to return to direct discharge, even using Type I standards.

Third, Type II devices are complex and very expensive. It is not possible to meet the standards for a Type II Device with only chlorination and maceration. In order to reach 150 mg/l or less suspended solids concentrations solids removal must be provided before maceration and chlorination and the effluent must pass through a centrifuge to remove any small particles remaining. This sludge that is collected must still be disposed of. It is commonly pumped ashore to sewers (Kaminsky, 1973). Since this waste is much more concentrated and is the source of sulfide generation, odor problems at terminals may be worse than they are now. This must be done on a routine basis, possibly several times per week, so there may not be a significant reduction in sewage charges. Based on the layout of the existing vessels, the modifications required, and additional equipment needed to have a certified Marine Sanitation Device, the cost is probably prohibitive when compared to other odor control alternatives with on-shore discharge. A similar type installation on a ferry in 1973 was reported to cost \$66,000 (Kaminsky, 1973). Other systems use on-board incineration of the sludge to avoid odor problems, but the ash must

still be taken ashore and disposed of. Operating costs for a 10,000 gpd system of this type may be as high as \$55.00 per day.

In summary then, overboard discharge may not be allowed if the state, with EPA approval, should so elect in the future. Type I devices, which probably could not be installed by the January 1978 deadline, represent no significant cost savings. Type II devices are very costly and may exacerbate the odor problems now experienced. Finally, return to overboard discharge would be a significant step backward from the policy of no discharge adopted by the ferry system in 1971. The ferry wastes would be discharged into surface waters of Puget Sound with potentially greater effects than the wastes would have after treatment in a municipal plant with discharge through a deep outfall line.

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