Removal of Hydrogen Sulfide from Ground Water in Central Florida

Thomas G. Lochrane
University of Central Florida

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REMOVAL OF HYDROGEN SULFIDE
FROM GROUND WATER IN CENTRAL FLORIDA

BY

THOMAS G. LOCHRANE, P.E.
B.S.C.E., NORWICH UNIVERSITY, 1968

RESEARCH REPORT

A Research Report presented in partial fulfillment
of the requirements for the degree
Master of Science
in the Graduate Studies Program of
Florida Technological University

Orlando, Florida
1977
ABSTRACT

REMOVAL OF HYDROGEN SULFIDE FROM GROUND WATER IN CENTRAL FLORIDA

by

Thomas Gene Lochrone, PE
B. S. C. E., Norwich University, 1968

The presence of hydrogen sulfide in a ground water source is noted by its rather obnoxious odor, similar to a "rotten egg". Concentrations as low as 0.05 ppm are noticeable, therefore, almost its entire removal is demanded prior to potable consumption. Hydrogen sulfide is formed primarily by the decomposition of organic matter in anaerobic conditions. Removal of this gas has been accomplished by means of aeration, detention, and chlorination over the years. The mechanisms behind each of these processes are complex and discussed in this paper.

During the course of this investigation, a literature survey concerning the nature and sources of hydrogen sulfide, its removal by aeration and detention, and the experimental methodology has been conducted. Samples were collected from two ground water locations in Central Florida; namely, City of Apopka Terrace Plant, and the City of Maitland Thistle Plant. These samples were taken before and after aeration and detained in containers.
similar to the storage tank dimensions. These samples were tested for Hydrogen Sulfide and pH with respect to time.

The aerators were determined to remove 13 to 15 percent $H_2S$, respectively. The pH values ranged between 7 - 8 prior to detention and rose slowly during $H_2S$ ionization to 8-8.6.

Both locations were evaluated to determine the most economic operating conditions. Ideally, Apopka should be removing between 30 - 40 percent by means of aeration, and Maitland, between 40 - 50 percent. Chlorination will remove the remaining $H_2S$.

Although the existing aerators were operating less than their optimum removal range, they should remain in service. This is based on deducting the aerator "sunk costs" from the economic evaluation.

Efforts should be encouraged to improve aerator efficiencies by increased agitation, contact time, and weir overflow rates in the aerator trays. These measures should increase the $H_2S$ reaction rate and improve its removal.

Detention only removes the odor problem, but the chlorine demand still remains, as exerted by the forms $HS^-$ and $S^2$. 
ACKNOWLEDGEMENTS

I would like to thank the Faculty and Staff at FTU for their helpful advice in the preparation of this report. I would especially like to thank Dr. Yousef A. Yousef for his technical guidance and Dr. Waldron M. McLellon for his excellent supervision of my entire graduate program.

Many thanks to my employer, Boyle Engineering Corporation, in particular H. W. Haeseker, PE, and other staff engineers for their guidance and understanding which made it possible for me to conduct my field testing at the case study locations.

Special praise is extended to both my typists: Rechea Hutchinson and Celeste Rycyk for their excellent work.

And finally, my everlasting gratitude to my wife Gloria, for all her love and understanding throughout my Master's Program.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. OBJECTIVES AND SCOPE</td>
<td>3</td>
</tr>
<tr>
<td>3. LITERATURE REVIEW</td>
<td>4</td>
</tr>
<tr>
<td>Sources and Nature of Hydrogen Sulfide</td>
<td></td>
</tr>
<tr>
<td>Removal by Aeration</td>
<td></td>
</tr>
<tr>
<td>Removal by Detention</td>
<td></td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td></td>
</tr>
<tr>
<td>Determination of Hydrogen Sulfide</td>
<td></td>
</tr>
<tr>
<td>Measurement of pH</td>
<td></td>
</tr>
<tr>
<td>Sample Collection</td>
<td></td>
</tr>
<tr>
<td>4. RESULTS AND DISCUSSION</td>
<td>31</td>
</tr>
<tr>
<td>Effect of Aeration</td>
<td></td>
</tr>
<tr>
<td>Effect of Detention</td>
<td></td>
</tr>
<tr>
<td>Effect of pH</td>
<td></td>
</tr>
<tr>
<td>5. CONCLUSIONS AND RECOMMENDATIONS</td>
<td>49</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>61</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>3-1.</td>
<td>Substances occurring in Natural Waters</td>
</tr>
<tr>
<td>3-2.</td>
<td>Solubilities of gases in pure water in contact with pure gas at 1 atm.</td>
</tr>
<tr>
<td>3-3.</td>
<td>Adsorption coefficients for H₂S and CO₂</td>
</tr>
<tr>
<td>3-4.</td>
<td>Hydrogen Sulfide factors</td>
</tr>
<tr>
<td>3-5.</td>
<td>Chlorine demanded by H₂S</td>
</tr>
<tr>
<td>4-1.</td>
<td>Aerator water storage characteristics</td>
</tr>
<tr>
<td>4-2.</td>
<td>Case study physical data</td>
</tr>
<tr>
<td>4-3.</td>
<td>H₂S removal and Reaction Rates during Aeration</td>
</tr>
<tr>
<td>4-4.</td>
<td>Calculated Contact time required for Aeration</td>
</tr>
<tr>
<td>4-5.</td>
<td>H₂S removed by ground storage tank Detention</td>
</tr>
<tr>
<td>4-6.</td>
<td>Reaction Rates during Detention</td>
</tr>
<tr>
<td>4-7.</td>
<td>pH trend during Detention</td>
</tr>
<tr>
<td>5-1.</td>
<td>Economic parameters for Aerator operations</td>
</tr>
<tr>
<td>5-2.</td>
<td>Estimated Aerator Annual Capital and Power Costs</td>
</tr>
<tr>
<td>5-3.</td>
<td>Proposed Aerators for H₂S removal</td>
</tr>
<tr>
<td>5-4.</td>
<td>Annual Cost evaluation of Aeration versus Chlorination</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Illustration Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Sulfur Cycle</td>
<td>9</td>
</tr>
<tr>
<td>3-2</td>
<td>Relationship between CO₂ and the three forms of Alkalinity at various pH Levels</td>
<td>22</td>
</tr>
<tr>
<td>3-3</td>
<td>Hydrogen Sulfide equilibrium curve</td>
<td>24</td>
</tr>
<tr>
<td>4-1</td>
<td>Typical ground storage tank with natural draft Aerator</td>
<td>32</td>
</tr>
<tr>
<td>4-2</td>
<td>Typical Crom natural draft Aerator</td>
<td>33</td>
</tr>
<tr>
<td>4-3</td>
<td>Aerator physical characteristics</td>
<td>34</td>
</tr>
<tr>
<td>4-4</td>
<td>Calculated Aerator Contact Time versus percent H₂S removal</td>
<td>40</td>
</tr>
<tr>
<td>4-5</td>
<td>Actual H₂S removal in ppm versus Detention Time</td>
<td>43</td>
</tr>
<tr>
<td>4-6</td>
<td>Actual H₂S removal in percent versus Detention Time</td>
<td>44</td>
</tr>
<tr>
<td>4-7</td>
<td>Rates of Reaction during Storage Tank Detention</td>
<td>46</td>
</tr>
<tr>
<td>4-8</td>
<td>Rates of Reaction during Storage Tank Detention</td>
<td>47</td>
</tr>
<tr>
<td>5-1</td>
<td>H₂S Removal in ppm and pH versus Detention Time for Apopka</td>
<td>50</td>
</tr>
<tr>
<td>5-2</td>
<td>H₂S Removal in ppm and pH versus Detention Time for Maitland</td>
<td>51</td>
</tr>
<tr>
<td>5-3</td>
<td>Annual Cost evaluation for H₂S removal by Aeration and Chlorination in Apopka</td>
<td>58</td>
</tr>
<tr>
<td>5-4</td>
<td>Annual Cost evaluation for H₂S removal by Aeration and Chlorination in Maitland</td>
<td>59</td>
</tr>
</tbody>
</table>
1.0 INTRODUCTION

The primary source of drinking water for the State of Florida is from deep wells which extend far into the limestone depths often referred to as the "Floridan Aquifer". These water sources are often troubled with the presence of hydrogen sulfide, which has a rather obnoxious odor somewhat like that of a "rotten egg". The removal of this constituent from the water is often accomplished by the use of both aeration and chlorination applications.

In the Central Florida area, as well as the State in general, water is stored in ground water reservoirs. These tanks often are constructed with natural draft aerators at their top. The water from the aquifer is pumped up through the aerator and allowed to flow by gravity over a series of cascading trays before reaching the tank below. It is during this process that the hydrogen sulfide is released from the water to the atmosphere. The effectiveness of this type of aerator is very important, since what is not released to the atmosphere must be removed by chlorination.

The Florida State Department of Environmental Regulation has suggested a maximum concentration for hydrogen sulfide in a potable water source at 0.05 ppm. This Agency does, however, require by law that all potable water sources maintain a free chlorine residual of 0.5 ppm. This latter requirement will entirely remove any hydrogen sulfide present in the water. Consequently, the chlorination criteria is sufficient enough to protect
the public from obnoxious sulfide odors in their drinking water.

The main consideration here is, therefore, an economic one. Since natural draft aerators have their limitations in sulfide removal from one source location to another, a methodology is required that will identify the most cost effective balance between aerator and chlorination treatment operations. Also, considerations need to be identified that will aid designers in upgrading existing aerator design to achieve maximum performance. The following report answers these questions, among others, in the removal of hydrogen sulfide from Central Florida water sources.
2.0 OBJECTIVE AND SCOPE

In the Central Florida area, a search for two rather average water supply locations was conducted. The City of Apopka, Terrace Water Plant, and the City of Maitland, Thistle Water Plant were selected as the typical case study locations.

The main objective of this research was to rate the effectiveness of natural draft aerators in operation; establish a methodology which would provide a means to identify the most cost effective combinations between chlorination and aeration; and to identify several aerator design considerations which would upgrade efficiency at existing and proposed locations in the removal of hydrogen sulfide.

The scope of this work was confined to natural draft cascade type aerators situated on top of reinforced concrete ground storage tanks. Both of these units were manufactured by the Crom Corporation, whose office is based in Gainesville, Florida. The aerator review was conducted solely on its ability to remove hydrogen sulfide and did not consider other constituents in the water that may cause other taste and odor problems.
3.0 LITERATURE REVIEW

The removal of hydrogen sulfide from ground water sources prior to potable consumption is often accomplished effectively by the processes of aeration, ionization and chlorination. The aeration process discussed herein uses the mechanism of a natural draft cascade type aerator situated on top a ground water storage tank which provides the means for detention and subsequent H₂S ionization. Chlorination is accomplished on the discharge side of the ground storage tank in advance of the water distribution system.

The effectiveness of each of these processes is rather complex and depends largely on the constituents and the H₂S concentration present in the raw water source. In order to evaluate the impact these constituents may have on the efficiency of each of the above processes, a clear understanding of the mechanisms behind each process is essential. In the report that follows, each process shall be researched with respect to hydrogen sulfide removal. Emphasis shall not only be placed on the theory of each process but also the parameters which significantly affect both the rate and direction of the removal process. And finally, all laboratory techniques, methods and equipment used in these determinations shall be presented.
3.1 Sources and Nature of Hydrogen Sulfide

Hydrogen Sulfide, $H_2S$, is found in ground water sources primarily as a result of the decomposition of organic matter containing sulfur and from the reduction of sulfites and sulfates, Metcalf and Eddy (1). Camp (2) lists in Table 3-1 substances that are most commonly present in natural water sources. Table 3-1 indicates that sulfates originate from minerals and the atmosphere; whereas, hydrogen sulfide, $H_2S$, and its ionic forms ($HS^-, S^-$), originate from the decomposition of organic matter.

Organic Sulfur is required in the synthesis of proteins and is released during degradation and then reduced into hydrogen sulfide under anaerobic conditions. Elemental sulfur ($S$) follows a different path. It is chemically reduced by oxidation to form the sulfate compound as $SO_4^-$ or $SO_3^-$. Sulfates are further reduced by bacteria under anaerobic conditions to form sulfites in the form of $SO_3^-$ or $SO_2$ and eventually sulfides as indicated by equations 1 and 2, Sawyer and McCarty (3).

\[ SO_4^- + \text{organic matter} \xrightarrow{\text{bacteria}} S^- + H_2O + CO_2 \quad \text{equation 1} \]
\[ S^- + 2H^+ \rightarrow H_2S (\uparrow) \quad \text{equation 2} \]

According to studies conducted by EPA (4), in this reaction 96 grams of sulfate ($SO_4^-$) make available 64 grams of oxygen leaving 32 grams of sulfide. This also indicates that about 42 grams of organic matter would be oxidized during the process.
<table>
<thead>
<tr>
<th>Origin</th>
<th>Suspended</th>
<th>Colloidal</th>
<th>Cases</th>
<th>Non-ionized solids and dipoles</th>
<th>Positive ions</th>
<th>Negative ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>From mineral soils and rocks</td>
<td>Clay, sand, other inorganic soils</td>
<td>Clay</td>
<td>SiO₂</td>
<td>Fe₂O₃</td>
<td>Al₂O₃</td>
<td>MnO₂</td>
</tr>
<tr>
<td>From the atmosphere</td>
<td></td>
<td>N₂</td>
<td>O₃</td>
<td>CO₂</td>
<td>SO₂</td>
<td></td>
</tr>
<tr>
<td>From organic decomposition</td>
<td>Organic soil (top soil), organic wastes</td>
<td>Vegetable coloring matter, organic wastes</td>
<td>CO₂</td>
<td>NH₃</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Living organisms</td>
<td>Fish, algae, diatoms, and minute animals</td>
<td>Viruses, bacteria, algae and diatoms</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The sulfate reducing bacteria (Desulfovibrio desulfuricans) exist in these anaerobic conditions and reduce sulfates and other sulfur compounds to hydrogen sulfide. Their optional growth range, with respect to pH units, has been determined to be within the limits 5.5 to 8.5. The optional temperature range corresponding to these pH conditions is from $24^\circ$ to $42^\circ$ C., White (5).

Another bacterial form which oxidizes sulfur compounds is from the genus Beggiatoa and Thiobacillus. The Beggiatoa are filamentous white sulfur bacteria that obtain the energy necessary for their growth by oxidizing the sulfide ion to colloidal sulfur, which is then stored in their cells, White (5).

According to Bass and Becking (6), the putrefaction of protein from bacterial action with sulfur compounds containing amino acids is another source of $H_2S$. Bacteria in the soil, water, intestines, and sewage, as indicated previously, decompose organic matter. This decomposition process yields protein, which contains sulfur from the three following forms of amino acids: cystine, cysteine, and methionione. These forms reduce to yield $H_2S$ by means of enzymes which are primarily Clostridium, Escherichia, Proteus, and Baccillus.

Postgate (7) indicates that bacteria can also synthesize sulfur containing amino acids from inorganic sulfates. In this case, the bacteria converts the sulfate ion to PAPS (3-phosphoadenosine - 5-phosphosulfate), also called active sulfate, and yields $H_2S$. PAPS, with an appropriate enzyme,
can convert sulfate to phenol, lipids, protein, and carbohydrates. These enzymes can be either Enterbacter aerogenes, Pseudomonas punctata, Clostridium kluyneri, Bakers yeast and Bacillus termenails.

According to Peck (8), dissimilatory sulfate reduction is conducted by a few types of bacteria under anaerobic conditions which can produce large amounts of $H_2S$. This reaction is characterized by APS formation. APS (Adenosine-5-phosphosulfate) is a nucleotide which differs from PAPS and is formed from ATP (Adenosine triphosphate) by the enzyme APS-sulfurylase. The APS reduces to yield $H_2S$.

The organisms which reduce APS in dissimilatory sulfate reduction are Desulfovibrio desulfuricans, Clostridium nigrificans, Vibrio-cholinicus, Thiobacillus theoparus, Thiobacillus throaxidaus and Thiobacillus denifrificans, as noted by Peck (8).

All of these biological reactions constitute part of what has been referred to as the "Sulfur Cycle". Sawyer and McCarty (3) have illustrated this cycle as noted in Figure 3-1. As exemplified by this illustration, these are several starting points from which the production of $H_2S$ may develop.

Hydrogen sulfide gas has a very obnoxious odor somewhat like that of a rotten egg. According to White (5), it is an almost impossible task to produce a water free of taste and odor at all times if $H_2S$ is present without some degree of treatment. As small as 0.5 ppm of $H_2S$ in cold water is
Fig. 3-1 (3)

SULFUR CYCLE
noticeable and the odor imparted by 1 ppm is definitely offensive. Less odor is detectable when the pH is high (8+). This would indicate the presence of alkaline sulfide (HS⁻, S⁻) which does not have the rotten egg odor related to H₂S, White (5). According to White (5), the minimal detectable taste in water is about 0.05 ppm.

The Florida Department of Environmental Regulation recommends a upper limit on hydrogen sulfide in potable drinking water at 0.05 ppm. However, since this agency requires all potable waters be chlorinated and have a 0.5 ppm free chlorine residual, the hydrogen sulfide will be removed by the chlorine. Consequently, the maximum level of H₂S in solution is not on their list of regulated levels. However, its presence does constitute a chlorine demand and therefore is of an economic concern.

Hydrogen sulfide can be related to the corrosion of water mains, sanitary sewer force mains and gravity lines since it can be converted to sulfuric acid when in the presence of oxygen by biological means. Equation 3 indicates the reaction that occurs, Metcalf and Eddy (1):

\[ H_2S + O_2 \xrightarrow{\text{bacteria}} H_2SO_4 \]  

It is the sulfuric acid that actually does the damage to the above systems. H₂S, or in solution hydrosulfuric acid, is a weaker acid than carbonic acid (CO₂) and has little affect on the above systems. As regards gravity or force main sewer lines partially full and with oxygen available, aerobic bacteria will oxidize the H₂S to sulfuric acid thus causing the decay
and ultimate damage.

The toxic conditions of $\text{H}_2\text{S}$ are mainly related to its release to the atmosphere. According to White (5), brief exposures to $\text{H}_2\text{S}$ gas, for 30 minutes or less, to concentrations as low as 0.1 percent by volume of air may be fatal. However, this concentration of 10,000 ppm is not normally associated with ground water sources.

Hydrogen sulfide is known to be a very explosive gas and as indicated above can be toxic. Associated symptoms from exposure to a toxic concentration are nausea, headaches, and dizziness. As noted by Fair, Geyer and Okun (9), at concentrations of approximately 500 ppm these symptoms may appear.

3.2 Removal by Aeration

Hydrogen sulfide, $\text{H}_2\text{S}$, is removed from a water source by means of aeration which utilizes the process of gas transfer. In gas transfer, molecules are exchanged between the liquid and a gas at a gas-liquid interface. This physical phenomenon according to Fair, Geyer and Okun (9), is accompanied with chemical, biochemical and biological, as well as biophysical changes.

The primary objectives of aeration in the removal of $\text{H}_2\text{S}$ as stated by Fair, Geyer and Okun (9) are:
(1) Eliminate objectionable tastes and odors.

(2) Reduce corrosion of metals, disintegration of concrete and cement.

(3) Reduce chlorine demands.

AWWA (10) cites gas transfer, by aeration, of a volatile material to or from water depends on several parameters which include but are not limited to the following:

(1) Temperature.

(2) Gas transfer resistance.

(3) Partial pressure of the gases in the aerator atmosphere.

(4) Turbulence in the gaseous and liquid state.

(5) Air-Volume ratio.

(6) Exposure time.

Aeration promotes equilibrium between the dissolved, volatile constituents in the liquid phase and those constituents present in the air with which it is exposed. The term equilibrium refers to a steady state condition, as regards the concentration of the dissolved substances.

In order to achieve this condition of equilibrium, AWWA (10) indicates sometimes long air-water exposure times are required. As a general rule, absolute equilibrium is seldom necessary or even economic. The main function of the aerator is to speed up the reaction rate of \( H_2S \), thereby releasing it to the atmosphere. This in turn reduces the overall chlorine
requirement and results in an economic savings.

The equilibrium, or saturated value of a dissolved gas, is an important characteristic which depends primarily upon the temperature of the water and the partial pressure of the gas in the atmosphere in contact with the water and dissolved solids. According to Henry's law, the higher the partial pressure, the greater the dissolved gas concentration. At a fixed partial pressure, the higher the temperature the lower the solubility or saturated value of a gas. These relationships have been noted by AWWA (10).

Weber (11) has stated this in other terms. Henry's law is a statement for dilute solutions at equilibrium, in which the concentration of a gas dissolved in a liquid is directly proportional to the partial pressure of that gas in the vapor phase with which the solution is in contact. Henry's law is expressed by equation 4 as follows:

\[ C_s = K_h p \]

\( C_s \) = saturation concentration of gas (ml/l)

\( K_h \) = coefficient of absorption (ml/r)

\( p \) = partial pressure (fraction %)

Nordell (12) has stated that the solubility of a gas is largely affected by increasing the temperature and the ionic impurities. Camp (2) provided Table 3-2, which shows the effect of temperature on gas solubility for several
Table 3-2

**SOLUBILITY OF GASES IN PURE WATER IN CONTACT WITH THE PURE GAS @ 1 ATM**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Nitrogen</th>
<th>Oxygen</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Carbon dioxide</th>
<th>Hydrogen sulfide</th>
<th>Sulfur dioxide</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98.81% N₂+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NH₃</td>
</tr>
<tr>
<td></td>
<td>[N₂]x10³ mg/l</td>
<td>[O₂]x10³ mg/l</td>
<td>[H₂]x10³ mg/l</td>
<td>[CH₄]x10³ mg/l</td>
<td>[CO₂]x10³ mg/l</td>
<td>[H₂S]x10³ mg/l</td>
<td>[SO₂]x10³ mg/l</td>
<td>[NH₃]x10³ mg/l</td>
</tr>
<tr>
<td>0</td>
<td>1.050</td>
<td>29.4</td>
<td>2.18</td>
<td>69.8</td>
<td>0.959</td>
<td>1.93</td>
<td>2.48</td>
<td>39.8</td>
</tr>
<tr>
<td>5</td>
<td>0.931</td>
<td>26.1</td>
<td>1.913</td>
<td>61.2</td>
<td>0.912</td>
<td>1.94</td>
<td>2.14</td>
<td>34.3</td>
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<tr>
<td>10</td>
<td>0.830</td>
<td>23.2</td>
<td>1.696</td>
<td>54.3</td>
<td>0.872</td>
<td>1.76</td>
<td>1.864</td>
<td>29.9</td>
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<tr>
<td>15</td>
<td>0.752</td>
<td>21.1</td>
<td>1.523</td>
<td>48.7</td>
<td>0.841</td>
<td>1.70</td>
<td>1.645</td>
<td>26.4</td>
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<td>20</td>
<td>0.689</td>
<td>19.3</td>
<td>1.384</td>
<td>44.3</td>
<td>0.812</td>
<td>1.64</td>
<td>1.475</td>
<td>23.6</td>
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<td>25</td>
<td>0.639</td>
<td>17.9</td>
<td>1.263</td>
<td>40.4</td>
<td>0.783</td>
<td>1.58</td>
<td>1.342</td>
<td>21.5</td>
</tr>
<tr>
<td>30</td>
<td>0.599</td>
<td>16.8</td>
<td>1.163</td>
<td>37.2</td>
<td>0.758</td>
<td>1.53</td>
<td>1.233</td>
<td>19.7</td>
</tr>
<tr>
<td>40</td>
<td>0.526</td>
<td>14.8</td>
<td>1.029</td>
<td>34.9</td>
<td>0.724</td>
<td>1.48</td>
<td>1.057</td>
<td>16.0</td>
</tr>
<tr>
<td>50</td>
<td>0.456</td>
<td>12.7</td>
<td>0.866</td>
<td>32.8</td>
<td>0.694</td>
<td>1.44</td>
<td>0.872</td>
<td>14.0</td>
</tr>
<tr>
<td>60</td>
<td>0.427</td>
<td>11.9</td>
<td>0.786</td>
<td>25.1</td>
<td>0.724</td>
<td>1.44</td>
<td>0.79</td>
<td>12.7</td>
</tr>
<tr>
<td>70</td>
<td>0.393</td>
<td>11.1</td>
<td>0.756</td>
<td>22.4</td>
<td>0.714</td>
<td>1.44</td>
<td>0.76</td>
<td>12.2</td>
</tr>
<tr>
<td>80</td>
<td>0.361</td>
<td>10.5</td>
<td>0.724</td>
<td>20.2</td>
<td>0.714</td>
<td>1.44</td>
<td>0.76</td>
<td>12.2</td>
</tr>
<tr>
<td>90</td>
<td>0.333</td>
<td>10.0</td>
<td>0.692</td>
<td>18.4</td>
<td>0.714</td>
<td>1.44</td>
<td>0.76</td>
<td>12.2</td>
</tr>
<tr>
<td>100</td>
<td>0.305</td>
<td>9.5</td>
<td>0.660</td>
<td>16.7</td>
<td>0.714</td>
<td>1.44</td>
<td>0.76</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Note: The table values are given in mg/l at 1 atm pressure.
This table enumerates the equilibrium concentrations of dissolved gases in pure water and its reaction products with the water at one (1) atmosphere.

The subscript (T) indicates solubilities, including ionization products. It is rather interesting to note that the solubility of $\text{H}_2\text{S}$ at 20°C is nearly twice that of carbonic acid ($\text{CO}_2$). This largely explains why the $\text{CO}_2$ is released to the atmosphere more readily than $\text{H}_2\text{S}$ during aeration.

AWWA (10) emphasizes that saturation values have significance in the analysis of gas transfer since it is the difference between it and the actual concentration in the water which establishes the driving force and rate of reaction. As for example, water deficient in oxygen when exposed to air will absorb oxygen from the atmosphere until equilibrium is reached. And if the water should be oversaturated with oxygen, it can be expected to release oxygen until equilibrium is released. The rate of the reaction is governed also by the distance the actual concentration is apart from equilibrium. This rate can be increased only by changing one of the several parameters cited previously by AWWA (10).

Lewis and Whitman (10) have a two film theory which cites that the boundary thickness between the liquid and gaseous state governs the rate of passage through them. Since the film thickness is a function of the kinematic viscosity, the rate of passage can be increased by agitation of the gas or liquid main body.
The Lewis and Whitman concept has been expressed as in equation 5 by AWWA (10).

\[
\frac{dm}{dt} = -D_g A \left( \frac{dc}{dy} \right)_1 = -D_L A \left( \frac{dc}{dy} \right)_2 = -D_e A \left( \frac{dc}{dy} \right)_3
\]
equation 5

\[
\left( \frac{dc}{dy} \right)_1 = \text{concentration gradient through the gas film.}
\]
\[
\left( \frac{dc}{dy} \right)_2 = \text{concentration gradient through the liquid film.}
\]
\[
\left( \frac{dc}{dy} \right)_3 = \text{concentration gradient in the body of the liquid below the liquid film.}
\]

\[D_g = \text{diffusion coefficient of gas through gas film.}\]
\[D_L = \text{diffusion coefficient of gas through liquid film.}\]
\[D_e = \text{diffusion eddy coefficient of the gas in the body of the liquid.}\]

This equation considers the eddy diffusion through the body of the liquid, in addition to molecular diffusion. The value of the eddy diffusion coefficient is the same order of magnitude as the eddy viscosity of the liquid. This largely depends on the hydraulic condition and the physical condition of the system, which in most cases prevails in a state of turbulent flow.

Since the eddy diffusion is much greater than the diffusivity through the liquid film, the gradient through the liquid is extremely small compared to the liquid film. Therefore, the dissolved gas throughout the depth of the liquid body may be considered uniform. The magnitude of the diffusivity in
the gas phase is greater than the liquid phase. Therefore, according to AWWA (10), the transfer of a sparingly soluble gas like oxygen, carbon dioxide, and hydrogen sulfide is controlled by the liquid film. This theory has been substantiated by Weber (11).

Since the concentration of the dissolved gas may be taken as uniform throughout the depth, the entire gradient is assumed to exist at the interface and is re-expressed according to AWWA (10) as follows:

\[
\frac{dm}{dt} = \frac{D_L}{Y_L} A (C_s - C_t) = K_L A (C_s - C_t) \quad \text{equation 6}
\]

\[K_L = \text{diffusivity (diffusion coefficient divided by the film thickness.)}\]

\[C_s = \text{saturation coefficient of gas in water.}\]

\[C_t = \text{concentration of gas in water after time (t).}\]

The above equation can further be managed to include the volume of the liquid (V) as indicated by AWWA (11) in equation 7:

\[
\frac{1}{V} \frac{dm}{dt} = \frac{dc}{dt} = K_L A \frac{V}{V} \left( C_s - C_t \right) \quad \text{equation 7}
\]

This can be interpreted to indicate that the rate of transfer at any time is proportional to the change in concentration. In gas release or desorption, the term \((C_s - C_t)\) will be negative reaching zero at equilibrium.

The rate of gas transfer is also proportional to the ratio of the interfacial area of the liquid volume and the transfer coefficient \((K_L)\). AWWA (10) further
indicates that since the interfacial areas are difficult to measure in some systems, an overall transfer coefficient, \( K_L a \), is used which yields the following expression in equation 8:

\[
\frac{dc}{dt} = K_L a (C_s - C_t) \quad \text{equation 8}
\]

\( a = \text{Area/Volume} \)

\( K_L a = \text{function of interfacial area, liquid volume, and chemical and physical variables.} \)

When this expression is integrated, the following expression results respective to adsorption and release:

**Gas Adsorption:**

\[
C_t = C_s - (C_s - C_o) \times 10^{-K_L a} \quad \text{equation 9}
\]

**Gas Release:**

\[
C_t = C_s + (C_o - C_s) \times 10^{-K_L a} \quad \text{equation 10}
\]

where, \( C_o = \text{initial concentration}. \)

According to Lewis and Whitman (10), the preceding equation can be interpreted into the following conclusions:

(1) Rate of gas transfer is directly proportional to gas saturation \( (C_s) \) and the actual concentration \( (C_t) \) in the water at any instance.

(2) Rate of gas transfer is directly proportional to the gas transfer coefficient, which depends upon the diffusivity of the gas and the film resistance.
(3) Rate of gas transfer is directly proportional to the exposed Area to Volume of water (A/V).

(4) Total amount of gas transfer is greater as the time of aeration is increased (contact time in aerator).

(5) The percent change in gas saturation deficit \( C_s - C_{t} \) or surplus \( C_t - C_s \) at any given time is constant based on the deficit or surplus at the beginning of the time period.

(6) Temperature and pressure are important since they influence the gas solubility \( C_s \). Temperature also influences the diffusivity and film resistance and hence the value of \( k \).

Lewis and Whitman (10) cite that as long as the product of area/volume to time remains constant, aerator performance remains constant. Therefore, if either the time factor or the area to volume ratio is increased, the efficiency should increase.
3.3 Removal by Detention

A chemical reaction occurs between the dissolved H₂S and its ionic forms in solution. During this process, the objectionable odors and tastes are removed, but the chlorine demand remains unchanged. As H₂S decreases in content, its ionic forms, HS⁻ and S⁻, increase. According to Fair, Geyer and Okun (9), these ionic forms cannot be removed by aeration.

Perhaps the two most significant constituents responsible for H₂S ionization are the hydrogen ion and CO₂ content. The hydrogen ion content, as indicated by the pH level, is considered the primary parameter. The CO₂ content is important in that its release causes a rise in the pH which tends to restrict the release of sulfide by promoting the ionization process.

According to Fair, Geyer and Okun (9), hydrogen sulfide has a very high solubility as compared to CO₂. This is exemplified by the fact that the adsorption coefficient for H₂S is nearly 2 to 3 times greater than that for CO₂.

Fair, Geyer and Okun (9) further indicate by table 3-3 that these adsorption coefficients are affected by temperature to a significant degree.

<table>
<thead>
<tr>
<th>Temp</th>
<th>H₂S</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C.</td>
<td>4690</td>
<td>1710</td>
</tr>
<tr>
<td>10°C.</td>
<td>3520</td>
<td>1190</td>
</tr>
<tr>
<td>20°C.</td>
<td>2670</td>
<td>898</td>
</tr>
</tbody>
</table>
According to Sawyer and McCarty (3), CO$_2$ is pH dependent like H$_2$S. CO$_2$ is normally found in natural water if the pH is less than 9. Above pH 9, the CO$_2$ moves into the alkaline forms, as indicated by Figure 3-2 based on a water having a total alkalinity of 100 mg/l @ 20°C.

Carbon dioxide has very often been used in advance of sulfur bearing waters to lower the pH level. According to C. C. Li (13), CO$_2$, in concentrations of about 10%, raises the hydrogen ion concentration significantly to favor the release of H$_2$S as a gas. However, if the CO$_2$ concentration naturally present in a water source is low, then it will have little impact at all in H$_2$S removal by aeration methods.

If CO$_2$ is present in significant amounts, Nordell (12) has cited that it will be released at a faster rate than the H$_2$S. As this occurs, the pH rises, thus causing the ionization of H$_2$S and decreases the efficiency of aeration methods of removal.

In aqueous solutions, hydrogen sulfide hydrolyzes as follows, according to White (5):

$$\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+ \quad \text{equation 11}$$

$$\text{HS}^- \rightarrow \text{S}^- + \text{H}^+ \quad \text{equation 12}$$

The hydrogen sulfide compound dissociates to hydrosulfide as HS$^-$ and further to S$^-$ in accordance with the hydrolysis constants indicated below by White (5):
RELATIONSHIP BETWEEN CO₂ AND THREE FORMS OF ALKALINITY AT VARIOUS pH LEVELS

(Based upon a water with a total alkalinity of 100 MG/L @ T = 25°C.)
\[ K = 9.1 \times 10^{-8} = \frac{(H^+) (HS^-)}{(H_2S)} \]

\[ K = 1.2 \times 10^{-12} = \frac{(H^+) (S^-)}{(HS^-)} \]

White (5) further indicates the effect of pH on the equilibrium of hydrogen sulfide and its ionic forms in Figure 3-3. This figure illustrates that at pH 7 the \( H_2S \) level is approximately 50 percent of the total dissolved sulfides; whereas, at pH 5 it is nearly 100 percent \( H_2S \). At pH 9, the \( H_2S \) content is nearly all hydrosulfide but starts to dissociate at pH 10 to the \( S^- \) ion as indicated by the equilibrium curve.

Pomeroy (12) has developed his own equilibrium curve based upon what he refers to as hydrogen sulfide factors. These factors represent percent \( H_2S \) present at certain pH levels. Table 3-4 lists these factors, which can be calculated from the hydrolysis constants cited above.

Table 3-4 (12)

<table>
<thead>
<tr>
<th>pH</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.98</td>
</tr>
<tr>
<td>6.0</td>
<td>0.86</td>
</tr>
<tr>
<td>6.5</td>
<td>0.67</td>
</tr>
<tr>
<td>7.0</td>
<td>0.39</td>
</tr>
<tr>
<td>7.5</td>
<td>0.17</td>
</tr>
<tr>
<td>8.0</td>
<td>0.06</td>
</tr>
<tr>
<td>9.0</td>
<td>0.0063</td>
</tr>
</tbody>
</table>

During detention, the \( H_2S \) present can also be oxidized by dissolved oxygen present in the water. Nordell (12) indicates that this process is
Fig. 3-3 (5)

HYDROGEN SULFIDE EQUILIBRIUM CURVE
(EFFECT OF pH ON HYDROGEN SULFIDE)
rather slow but does produce colloidal sulfur that can be visually noticed in the water. White (5) indicates this occurrence by equation 13.

$$H_2S + O_2 \rightarrow H_2O + S^0$$  equation 13

Both hydrogen sulfide and its ionic forms are eventually removed from the water by chlorination. Tank detention only provides the $H_2S$ time to dissociate, which when in its ionic forms $HS^-$ and $S^-$ have no taste or odor problems. With the addition of chlorine primarily to disinfect the water for potable consumption, an added demand still exists from dissociated $H_2S$.

There are basically two reactions that occur between $H_2S$ and chlorine as indicated by equations 14 and 15.

$$H_2S + Cl_2 = 2HCL + S^0$$  equation 14

$$H_2S + 4Cl_2 + 4H_2O = H_2SO_4 + 8HCL$$  equation 15

Theoretically, equation 14 should only demand 2.1 pounds of chlorine to one pound of $H_2S$, and equation 15 only 8.4 pounds of chlorine to 1.0 pound of $H_2S$, according to White (5). In equation 14, elemental sulfur and water are produced by controlled chlorine addition. This is often accomplished in advance of water treatment facilities which pre-chlorinate. The elemental sulfur is then collected in the filters of the plant rather than being discharged in the distribution system for consumption.

Normally, quantities of chlorine greater than that required by $H_2S$ are added to obtain a free chlorine residual after disinfection requirements. This causes equation 15 to govern the chlorine demands for $H_2S$ removal,
as verified by FMC (14). White (5) further points out that if excessive chlorination occurs to a sulfur bearing water, colloidal sulfur will be formed which will appear as a milky blue turbidity.

As regards the oxidation of the alkaline sulfide forms, experiments by Choppin and Faulkenberry indicate that it is not simple and direct and may yield polysulfides, sulfites and thiosulfates, in addition to elemental sulfur and sulfates, White (5). Evidence of this is noticed by hot water systems which have a noticeable odor. This is not \( \text{H}_2\text{S} \) but rather sulfurous odor. Monscvitz and Ainsworth attribute this demonstrated odor to polysulfides \( (\text{H}_2\text{S}_n) \) in oxidation with \( \text{H}_2\text{S} \), White (5). In a collection system it is possible for these polysulfides to revert back to \( \text{H}_2\text{S} \), as indicated by White (5).

According to Monscvitz and Ainsworth, the solution here is to convert the colloidal sulfur and polysulfides to sulfates by first adding sulfite, White (5). This forms thiosulfate \( (\text{S}_2\text{O}_3) \) which can be converted to sulfate by rechlorination as follows in White's (5) equations:

\[
\begin{align*}
\text{SO}^0 + \text{SO}_3^{-} & \quad \rightarrow \quad \text{S}_2\text{O}_3^- \\
\text{HS}_n^- & \\
\text{S}_2\text{O}_3^- + \text{HOCL} & \quad \rightarrow \quad \text{S}_4\text{O}_6^{=+} + \text{SO}_4^{=+} \\
\end{align*}
\]

Equation 16 is rapid, whereas 17 is not. The tetrathionate \( (\text{S}_4\text{O}_6^{=}) \) rapidly converts to sulfates which have no odor. This dechlorination process is completed by the addition of sulfur dioxide.
Table 3-5

CHLORINE DEMANDED BY HYDROGEN SULFIDE

<table>
<thead>
<tr>
<th>Source</th>
<th>Theoretical</th>
<th>Actual Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂S to Sulfate (EQ 15)</td>
<td>H₂S to Sulfur/Water (EQ 14)</td>
</tr>
<tr>
<td>White</td>
<td>8.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Betz</td>
<td>8.4</td>
<td>2.1</td>
</tr>
<tr>
<td>E. K. Gilbert</td>
<td>8.37</td>
<td>2.08</td>
</tr>
<tr>
<td>EPA</td>
<td>8.87</td>
<td>2.22</td>
</tr>
<tr>
<td>Nordell</td>
<td>8.32</td>
<td>2.08</td>
</tr>
</tbody>
</table>
According to many sources of information, the chlorine demand exerted by $H_2S$ and its ionic forms differs from the theoretical requirements, as cited in Table 3-5. In review of the actual demands verses theoretical, it appears as though an average of 10 parts of chlorine are demanded to remove 1 part of $H_2S$.

3.4 Experimental Procedures

3.4.1 Determination of Hydrogen Sulfide

There are currently two accepted methods for the determination of hydrogen sulfide as follows:

1) Photometric Method.

2) Titration Method.

Both of these methods use the methylene blue concept. The titration method is a colorimetric method which, according to Standard Methods (15), is based on the chemical reaction between paraaminodimethylaniline, ferric chloride and the sulfide ion to form a blue color.

This titration method is considered the most accurate method in the determination of $H_2S$. Since hydrogen sulfide begins to dissociate rather slowly, but faster when agitated or moved, this test is normally conducted in the field at the specific collection location. The titration test is considered to be accurate within 10%.
The photometric method is conducted with the use of a colorimeter or spectrophotometer. This method was selected for the \( \text{H}_2\text{S} \) field determination. The equipment used was a HACH DC-DR kit field laboratory colorimeter with a glass filter of wavelength 665 nm. In this method, light is passed through a sample of the water and the filter, during which a reading is indicated on a scale. The scale needs to be calibrated to a stock solution of known concentrations for accurate conversions. This method is claimed by the Hach Testing Company to measure accurately within 10%+; however, most professional laboratories use the titration method over the Hach kit.

3.4.2 Measurement of pH

The other parameter of interest in this study was the pH level during the test. This was accomplished by means of pH probe-type meters, calibrated to a buffer solution of pH 7 in advance and during the testing period.

3.4.3 Collection Procedures and Methodology

Grab samples were collected at two specific locations at the respective locations as follows:

(1) A nonaerated sample was gathered from a tap situated on the discharge piping downstream from the well pump.

(2) An aerated sample was gathered from the bottom of the curb in the aerator prior to entering the storage tank.
Both of these samples were carefully moved to an adjacent building out of direct sunlight and tested for pH and $\text{H}_2\text{S}$ every 15 minutes. See Table 4-5.
4.0 RESULTS AND DISCUSSION

4.1 Effect of Aeration

The aerators situated at both of the test locations are natural draft cascade type aerators as manufactured by the Crom Corporation. Figure 4-1 pictures a typical ground storage tank and aerator similar to those investigated. Figure 4-2 is a close-up of the aerator, indicating the fiberglass tray design and actual arrangement. Figure 4-3 further provides more detailed physical characteristics of the aerator and its components at various sizes.

The field $\text{H}_2\text{S}$ tests indicated that raw water concentration in Apopka and Maitland were 1.78 and 1.05 ppm, respectively. After aeration, the $\text{H}_2\text{S}$ concentrations were decreased to 1.55 and 0.90 ppm, which represents removals of 12.92 and 14.29 percent, respectively. These data are summarized in Table 4-3.

According to the physical data listed in Table 4-2 for these case study locations, contact times were calculated for each aerator corresponding to actual flow rates delivered from their wells. Apopka detained its well water in the aerator for 43 seconds; whereas, Maitland, for only 21 seconds. Table 4-1 lists storage volumes for aerators of various sizes from which this contact time was calculated.

From these actual data collected during $\text{H}_2\text{S}$ removal by detention, it was determined that the dissociation rate of $\text{H}_2\text{S}$ removal followed a first order
Fig. 4-1
TYPICAL GROUND STORAGE TANK WITH NATURAL DRAFT CASCADE TYPE AERATOR
Fig. 4-2

Typical CROM natural draft aerator. Screening has been partially removed to provide clear view of interior.
**Fig. 4-3**

**AERATOR PHYSICAL CHARACTERISTICS**

![Diagram of an aerator with labels for TRAYS, CAST IRON INFLUENT PIPE, and CIRCULAR CURB.]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>12&quot;</td>
<td>4'9&quot;</td>
<td>12'8&quot;</td>
<td>8'8&quot;</td>
<td>24</td>
<td>350</td>
<td>850</td>
</tr>
<tr>
<td>1800</td>
<td>12&quot;</td>
<td>5'6&quot;</td>
<td>15'0&quot;</td>
<td>11'0&quot;</td>
<td>24</td>
<td>850</td>
<td>2400</td>
</tr>
<tr>
<td>2500</td>
<td>14&quot;</td>
<td>5'6&quot;</td>
<td>17'4&quot;</td>
<td>13'4&quot;</td>
<td>24</td>
<td>1200</td>
<td>3500</td>
</tr>
<tr>
<td>3500</td>
<td>16&quot;</td>
<td>6'3&quot;</td>
<td>21'8&quot;</td>
<td>17'8&quot;</td>
<td>24</td>
<td>1750</td>
<td>5000</td>
</tr>
<tr>
<td>5000</td>
<td>20&quot;</td>
<td>6'3&quot;</td>
<td>28'0&quot;</td>
<td>23'4&quot;</td>
<td>24</td>
<td>2400</td>
<td>7300</td>
</tr>
</tbody>
</table>
Table 4-1

AERATOR WATER STORAGE CHARACTERISTICS

<table>
<thead>
<tr>
<th>Aerator Capacity (GPM)</th>
<th>Number Of Levels</th>
<th>Total Trays</th>
<th>Total Storage In Aerator (GAL)(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>4</td>
<td>24</td>
<td>300</td>
</tr>
<tr>
<td>1800</td>
<td>4</td>
<td>24</td>
<td>600</td>
</tr>
<tr>
<td>2500</td>
<td>4</td>
<td>24</td>
<td>900</td>
</tr>
<tr>
<td>3500</td>
<td>4</td>
<td>24</td>
<td>1500</td>
</tr>
<tr>
<td>5000</td>
<td>4</td>
<td>24</td>
<td>2600</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>5</td>
<td>30</td>
<td>2840</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>6</td>
<td>36</td>
<td>3080</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>7</td>
<td>42</td>
<td>3320</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>9</td>
<td>54</td>
<td>3560</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>11</td>
<td>68</td>
<td>3800</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>13</td>
<td>80</td>
<td>4040</td>
</tr>
<tr>
<td>5000 (1)</td>
<td>15</td>
<td>92</td>
<td>4280</td>
</tr>
</tbody>
</table>

(1) Assumed configuration based on stacking trays vertically.

(2) Calculations based on volume in trays with (1) one inch overflow, and (6) six inches water depth in curb prior to tank entry.
Table 4-2

CASE STUDY PHYSICAL DATA

<table>
<thead>
<tr>
<th>ITEM</th>
<th>APOPKA</th>
<th>MAITLAND</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification</td>
<td>Terrace Plant</td>
<td>Thistle Plant</td>
</tr>
<tr>
<td>Ground Storage Tank Size (Gallons)</td>
<td>500,000</td>
<td>350,000</td>
</tr>
<tr>
<td>Aerator Size (GPM)</td>
<td>2500</td>
<td>1800</td>
</tr>
<tr>
<td>Well Discharge Rate (GPM)</td>
<td>1260</td>
<td>1700</td>
</tr>
<tr>
<td>Length of Weir (ft.)</td>
<td>178.5</td>
<td>128.5</td>
</tr>
<tr>
<td>Weir Overflow Rate (GPM/ft.)</td>
<td>7.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Volume of Water (Gal.) In Aerator and Curb</td>
<td>900</td>
<td>600</td>
</tr>
<tr>
<td>Calculated aerator (1) Contact time (sec.)</td>
<td>43</td>
<td>21</td>
</tr>
</tbody>
</table>

(1) Based on Fig. 4-7 and Fig. 4-8
Table 4-3

$H_2S$ REMOVAL AND REACTION RATES DURING AERATION

<table>
<thead>
<tr>
<th>ITEM</th>
<th>APOPKA</th>
<th>MAITLAND</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2S$ present in raw water (ppm)</td>
<td>1.78</td>
<td>1.05</td>
</tr>
<tr>
<td>$H_2S$ present after aeration (ppm)</td>
<td>1.55</td>
<td>0.90</td>
</tr>
<tr>
<td>$H_2S$ removed (ppm) (percent)</td>
<td>0.23</td>
<td>0.15</td>
</tr>
<tr>
<td>Calculated $H_2S$ Reaction Rate by Aeration (min$^{-1}$)</td>
<td>$1.94 \times 10^{-1}$</td>
<td>$4.36 \times 10^{-1}$</td>
</tr>
</tbody>
</table>


reaction. AWWA (10) cites that CO₂ is removed during multiple tray aeration, according to a first order reaction. Therefore, based on these facts H₂S was considered to follow a first order reaction during aeration. Corresponding reaction rates were determined per location with respect to the actual H₂S removal. Table 4-3 lists both these calculated reaction rates and the respective H₂S removals.

The reaction rate for a first order reaction plots a straight line on semi-log paper and conforms to the following equation:

\[ KT = k = 2.303 \log \frac{a}{a-x} \]

where:

- \( K \) = reaction rate (min⁻¹)
- \( T \) = contact time (min)
- \( k \) = fraction
- \( a \) = initial concentration (ppm)
- \( x \) = removed concentration (ppm)
- \( a-x \) = remaining concentration (ppm)

Using the calculated reaction rates and contact time for each aerator, a relationship was plotted for the theoretical contact times required at different hydrogen sulfide removals. This was developed for the Apopka and Maitland aerators, assuming the weir overflow rates were held constant. These results were plotted as Figure 4-4.
### Table 4-4

**CALCULATED CONTACT TIME REQUIRED FOR AERATION**

<table>
<thead>
<tr>
<th>Percent $\text{H}_2\text{S}$ Removed (%)</th>
<th>Calculated Contact Time (min.)</th>
<th>Maitland $(K_{\text{MA}} = 4.36 \times 10^{-1} \text{min}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>Apopka</em> $(K_{\text{AA}} = 1.94 \times 10^{-1} \text{min}^{-1})$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.54</td>
<td>0.24</td>
</tr>
<tr>
<td>12.92</td>
<td>0.71</td>
<td>---</td>
</tr>
<tr>
<td>14.92</td>
<td>---</td>
<td>0.35</td>
</tr>
<tr>
<td>15</td>
<td>0.84</td>
<td>0.37</td>
</tr>
<tr>
<td>20</td>
<td>1.15</td>
<td>0.51</td>
</tr>
<tr>
<td>25</td>
<td>1.48</td>
<td>0.66</td>
</tr>
<tr>
<td>30</td>
<td>1.84</td>
<td>0.81</td>
</tr>
<tr>
<td>35</td>
<td>2.22</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>2.63</td>
<td>1.17</td>
</tr>
<tr>
<td>45</td>
<td>3.08</td>
<td>1.37</td>
</tr>
<tr>
<td>50</td>
<td>3.57</td>
<td>1.60</td>
</tr>
<tr>
<td>55</td>
<td>4.11</td>
<td>1.83</td>
</tr>
<tr>
<td>60</td>
<td>4.72</td>
<td>2.10</td>
</tr>
<tr>
<td>70</td>
<td>6.21</td>
<td>2.76</td>
</tr>
<tr>
<td>80</td>
<td>8.30</td>
<td>3.69</td>
</tr>
<tr>
<td>90</td>
<td>11.86</td>
<td>5.28</td>
</tr>
<tr>
<td>95</td>
<td>15.44</td>
<td>6.87</td>
</tr>
<tr>
<td>96</td>
<td>16.59</td>
<td>7.38</td>
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<tr>
<td>97</td>
<td>18.08</td>
<td>8.04</td>
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<td>98</td>
<td>20.17</td>
<td>8.97</td>
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<td>99</td>
<td>23.74</td>
<td>10.56</td>
</tr>
<tr>
<td>99.9</td>
<td>35.61</td>
<td>15.84</td>
</tr>
<tr>
<td>99.99</td>
<td>47.48</td>
<td>21.12</td>
</tr>
</tbody>
</table>

@ $T = 20^\circ \text{C}$
Fig. 4-4

CALCULATED AERATOR CONTACT TIME VERSUS PERCENT H₂S REMOVAL

0.1  1.0  10  100

10  1.0  0.1

Calculated Contact Time (Min)

Maitland

Apopka

% H₂S Removed

T = 20°C
4.2 Effect of Detention

The main effect of detention on the aerated and non-aerated waters was to decrease the H$_2$S concentration. The actual H$_2$S concentrations are listed in Table 4-5 with respect to simulated ground storage tank detention time. These data are graphically presented in terms of percent H$_2$S removed and actual H$_2$S concentration remaining versus time, in Figures 4-5 and 4-6.

These results, when plotted on semi-log paper, approximate a straight line, thus indicating a first order reaction has occurred. Figures 4-7 and 4-8 indicate the plots for both case study locations. Their respective reaction rates (K) are listed in Table 4-6 for aerated and non-aerated water as determined by equation 18.

As the H$_2$S concentration decreased, a noticeable reduction in odor was experienced. At concentrations of approximately 0.05 ppm and less, hardly any odor could be detected. This observation, supported by previous research, indicates that the ionization of H$_2$S had occurred during detention.

4.3 Effect of pH

The pH was noted to increase during the detention time of the aerated and non-aerated water, as listed in Table 4-7. This pH was a very slow process. As for example, Apopka waters only increased 0.7 of a pH unit in 6.5 hours, and in Maitland the increase was about 0.8 of a pH unit in 4.5 hours. This slightly faster pH rate corresponds to a slightly higher rate of reaction indicated in Table 4-6 for Maitland.
Table 4-5

$H_2S$ REMOVED BY GROUND STORAGE TANK DETENTION

<table>
<thead>
<tr>
<th>Measured Detention Time (Min)</th>
<th>Apopka</th>
<th></th>
<th></th>
<th>Maitland</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2S$ Raw (2)</td>
<td>Percent Removed (%)</td>
<td>$H_2S$ Atr (1)</td>
<td>Percent Removed (%)</td>
<td>$H_2S$ Raw (2)</td>
<td>Percent Removed (%)</td>
</tr>
<tr>
<td>0</td>
<td>1.78</td>
<td>0</td>
<td>1.55</td>
<td>0</td>
<td>1.05</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>1.40</td>
<td>20.0</td>
<td>1.42</td>
<td>8.4</td>
<td>0.97</td>
<td>7.6</td>
</tr>
<tr>
<td>60</td>
<td>1.11</td>
<td>36.5</td>
<td>1.31</td>
<td>15.5</td>
<td>0.74</td>
<td>29.5</td>
</tr>
<tr>
<td>90</td>
<td>0.90</td>
<td>48.5</td>
<td>1.22</td>
<td>21.3</td>
<td>0.62</td>
<td>40.9</td>
</tr>
<tr>
<td>120</td>
<td>0.82</td>
<td>53.1</td>
<td>1.05</td>
<td>32.3</td>
<td>0.51</td>
<td>51.4</td>
</tr>
<tr>
<td>150</td>
<td>0.67</td>
<td>61.7</td>
<td>0.82</td>
<td>47.1</td>
<td>0.36</td>
<td>65.7</td>
</tr>
<tr>
<td>180</td>
<td>0.54</td>
<td>69.1</td>
<td>0.60</td>
<td>61.3</td>
<td>0.28</td>
<td>73.3</td>
</tr>
<tr>
<td>210</td>
<td>0.44</td>
<td>74.9</td>
<td>0.51</td>
<td>67.1</td>
<td>0.23</td>
<td>78.1</td>
</tr>
<tr>
<td>240</td>
<td>0.32</td>
<td>81.7</td>
<td>0.41</td>
<td>73.5</td>
<td>0.16</td>
<td>84.8</td>
</tr>
<tr>
<td>270</td>
<td>0.20</td>
<td>88.6</td>
<td>0.26</td>
<td>83.2</td>
<td>0.11</td>
<td>89.5</td>
</tr>
<tr>
<td>300</td>
<td>0.17</td>
<td>90.3</td>
<td>0.20</td>
<td>87.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>0.14</td>
<td>92.0</td>
<td>0.15</td>
<td>90.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>0.10</td>
<td>94.3</td>
<td>0.13</td>
<td>91.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>0.08</td>
<td>95.4</td>
<td>0.09</td>
<td>94.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$@ T = 20^\circ C$

(1) Aerated Sample
(2) Non-Aerated Sample
Fig. 4-5

ACTUAL HYDROGEN SULFIDE REMOVED CONCENTRATION VERSUS TIME @ T = 20° C
Fig. 4-6

ACTUAL HYDROGEN SULFIDE REMOVED
PERCENT VERSUS TIME
@ T = 20° C

Detention Time (Min)

Percent Hydrogen Sulfide Removed (%)

- Apopka
- Maitland
- Non-Aerated
- Aerated
### Table 4-6

**REACTION RATES DURING DETENTION**

<table>
<thead>
<tr>
<th>Location</th>
<th>Source</th>
<th>Apopka (Min)⁻¹</th>
<th>Maitland (Min)⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated</td>
<td></td>
<td>7.69x10⁻³ (K_AA)</td>
<td>9.09x10⁻³ (K_MA)</td>
</tr>
<tr>
<td>Non-Aerated</td>
<td></td>
<td>7.41x10⁻³ (K_ANA)</td>
<td>8.70x10⁻³ (K_MNA)</td>
</tr>
</tbody>
</table>

@ T = 20° C

\[
K = \text{Reaction Rate} = \frac{k}{t} = 2.303 \log \left( \frac{a}{x} \right)
\]

where:
- \(a\) = initial \(H_2S\) concentration
- \(x\) = removed \(H_2S\) concentration
- \(a-x\) = remaining \(H_2S\) concentration
Fig. 4-7
APOPKA
RATES OF REACTION DURING STORAGE TANK DETENTION

\[ k = 2.303 \log \left( \frac{a}{a-x} \right) \]

Rate of Reaction
\[ K_{\text{ANA}} = \]
7.41 x 10^{-3} min^{-1}
\[ K_{\text{AA}} = \]
7.69 x 10^{-3} min^{-1}

- Non-Aerated
- Aerated
@ T = 20° C
RATES OF REACTION DURING STORAGE TANK DETENTION

Fig. 4-8

MAITLAND

RATES OF REACTION

K_{MNA} = 6.70 \times 10^{-3} \text{ min}^{-1}
K_{MA} = 9.09 \times 10^{-3} \text{ min}^{-1}

Non-Aerated

\text{T} = 20^\circ C

(\frac{x - a}{d}) = 2.903 \log \frac{k}{2}
<table>
<thead>
<tr>
<th>Detention Time (min)</th>
<th>Apopka</th>
<th></th>
<th>Maitland</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-Aerated</td>
<td>Aerated</td>
<td>Non-Aerated</td>
<td>Aerated</td>
</tr>
<tr>
<td>0</td>
<td>~~~~</td>
<td>~~~~</td>
<td>~~~~</td>
<td>~~~~</td>
</tr>
<tr>
<td>30</td>
<td>7.81</td>
<td>7.94</td>
<td>7.10</td>
<td>7.20</td>
</tr>
<tr>
<td>60</td>
<td>7.83</td>
<td>7.97</td>
<td>7.45</td>
<td>7.52</td>
</tr>
<tr>
<td>90</td>
<td>7.86</td>
<td>8.02</td>
<td>7.62</td>
<td>7.64</td>
</tr>
<tr>
<td>120</td>
<td>7.90</td>
<td>8.06</td>
<td>7.70</td>
<td>7.72</td>
</tr>
<tr>
<td>150</td>
<td>8.00</td>
<td>8.14</td>
<td>7.76</td>
<td>7.78</td>
</tr>
<tr>
<td>180</td>
<td>8.09</td>
<td>8.22</td>
<td>7.81</td>
<td>7.82</td>
</tr>
<tr>
<td>210</td>
<td>8.16</td>
<td>8.32</td>
<td>7.86</td>
<td>7.88</td>
</tr>
<tr>
<td>240</td>
<td>8.25</td>
<td>8.39</td>
<td>7.92</td>
<td>7.93</td>
</tr>
<tr>
<td>270</td>
<td>8.33</td>
<td>8.45</td>
<td>7.96</td>
<td>7.98</td>
</tr>
<tr>
<td>300</td>
<td>8.39</td>
<td>8.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>8.43</td>
<td>8.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>8.47</td>
<td>8.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>8.50</td>
<td>8.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

@ T = 20° C
5.0 CONCLUSIONS AND RECOMMENDATIONS

The actual concentrations of \( \text{H}_2\text{S} \) and pH levels with respect to detention time are consolidated on one plot for both case study locations. Figure 5-1 represents Apopka and 5-2, Maitland. In observation of these figures, the following conclusions can be noted:

1. \( \text{H}_2\text{S} \) concentration decreases, the pH increases.
2. \( \text{H}_2\text{S} \) dissociates slowly during detention.
3. pH changes slowly during detention.

As the \( \text{H}_2\text{S} \) ionizes to \( \text{HS}^- \) and \( \text{S}^2- \), the taste and odor decrease, but the chlorine demand remains. Since regulatory agencies require a free chlorine residual of 0.5 ppm, the chlorine demand exerted by the ionic \( \text{H}_2\text{S} \) form will be satisfied.

The net result of this situation is increased chlorine costs for total treatment. From this point, the advantage of aeration should become readily apparent. If the \( \text{H}_2\text{S} \) is released as a gas to the atmosphere, then it will not be present in solutions to exert a chlorine demand. Therefore, maximum efficiency of the aerator is desirable.

In order to determine the most cost effective balance between aeration and chlorination costs, an economic evaluation is necessary. Therefore, the following methodology was developed to identify this condition in terms of a desired aerator efficiency range for Apopka and
Fig. 5-1
APOPKA
H₂S REMOVAL AND pH TRENDS

H₂S Concentration (PPM)

Detention Time (Min)

@ T = 20°C

Non-Aerated
Aerated

Δ pH
Θ H₂S
Fig. 5-2
MAITLAND
H₂S REMOVAL AND pH TRENDS

H₂S Concentration (PPM)

PH

0.0  0.5  1.0  1.5

Detention Time (Min)

0  100  200  300  400

Non-Aerated

Aerated

@ T = 20° C

H₂S
Table 5-1
ECONOMIC PARAMETERS FOR AERATOR OPERATIONS

<table>
<thead>
<tr>
<th>Item</th>
<th>Apopka</th>
<th>Maitland</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerator Capacity (GPM)</td>
<td>2500</td>
<td>1800</td>
</tr>
<tr>
<td>Aerator Initial Cast ($)</td>
<td>7000</td>
<td>6000</td>
</tr>
<tr>
<td>Annual OR&amp;M Cost ($) (12 hrs. @ $2.50)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Annual Power Cost ($) (@ $0.04/kw-hr.)</td>
<td>780(1) ($65/static ft)</td>
<td>630(1) ($52.5/static ft)</td>
</tr>
<tr>
<td>Present Worth of Total Costs (P/A, 6, 30) = 13.77 ($)</td>
<td>18150</td>
<td>15100</td>
</tr>
<tr>
<td>Equivalent uniform annual total cost (A/P, 6, 30) = 0.07265 ($)</td>
<td>1320</td>
<td>1100</td>
</tr>
</tbody>
</table>

(1) Based on 12 Ft. static head above water level in ground storage tank.
Maitland.

The chlorination costs were calculated based on chlorine gas at $350 per one-ton cylinder. These resulting costs appear in Table 5-4 expressed as annual costs.

The aerators at both locations are in-place, so a hypothetical situation was developed which considered both aerators non-existent. Table 5-1 lists the parameters of concern in aerator operations as:

1. Aerator Capital Cost.
2. Operation Repair and Maintenance (OR&M) Costs.

These costs were converted to a present worth value based on a thirty year service life and the value of money at 6 percent. The present worth value was then spread out over the thirty year period on a uniform annual cost basis.

In order to determine the annual capital costs for aerators to achieve certain H₂S percent removals, we referred back to the calculated contact times for H₂S removal listed in Table 4-4. From these data and the volume of storage available in each aerator size, the increased contact times were met. This approach assumes that the weir overflow rate remains constant by decreasing the length of weirs per tray.

As part of this approach, the aerators were selected until the largest standard unit was reached. Beyond this point, trays were stacked by levels
of one each, thus increasing the height by 1.5'. The resulting increased aerator capital cost was estimated at $3250 per level. This rise in height also increased power costs. Table 5-3 indicated the theoretical required contact times and the aerator design which meets this requirement. Table 5-2 lists aerator capital and power costs.

In Table 5-4, annual chlorination and aerator costs are listed individually and combined. By plotting the combined costs at different percentages of H₂S removed, an economic range can be identified. This range indicates the most cost effective H₂S removal percentage for combined aeration and chlorination treatment methods. Figures 5-3 and 5-4 are graphical representation of these annual costs. This economic range is noted at the sag in the combined cost curve.

These results indicate that a larger aerator, at both Apopka and Maitland, would be more cost effective in the removal of H₂S if the reaction rates cannot be increased. The preferred H₂S percent removal by means of aeration is indicated as follows:

- Apopka: 30 - 40% H₂S Removal
- Maitland: 40 - 50% H₂S Removal

This synthetic evaluation of preferred aerator efficiencies at these locations indicates that the aerators are currently operating at less than their optimal level for the most cost effective operations. The aerators are only removing from 13 - 15 percent H₂S by weight.
<table>
<thead>
<tr>
<th>Aerator Capacity—GPM (# Tray Levels)</th>
<th>Capital Costs($)</th>
<th>Annual Capital Costs($) (A/P, 6, 30) (2)</th>
<th>Apopka Annual Power Cost($) (3)</th>
<th>Maitland Annual Power Cost($) (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5000</td>
<td>360</td>
<td>780</td>
<td>630</td>
</tr>
<tr>
<td>1800</td>
<td>6000</td>
<td>435</td>
<td>780</td>
<td>630</td>
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<td>2500</td>
<td>7000</td>
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<td>630</td>
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<td>3500</td>
<td>9500</td>
<td>690</td>
<td>780</td>
<td>630</td>
</tr>
<tr>
<td>5000 (4)</td>
<td>13000</td>
<td>945</td>
<td>878</td>
<td>709</td>
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<td>5000 (5)</td>
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<td>5000 (8)</td>
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<td>1890</td>
<td>1268</td>
<td>1023</td>
</tr>
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<td>5000 (9)</td>
<td>29250</td>
<td>2125</td>
<td>1365</td>
<td>1102</td>
</tr>
<tr>
<td>5000 (10)</td>
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<td>1463</td>
<td>1180</td>
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<td>35750</td>
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<td>1496</td>
</tr>
<tr>
<td>5000 (15)</td>
<td>48750</td>
<td>3540</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Aerator height increased 1.5' per tray and estimated at $3250/tray.
(2) 0.07265 = annual cost factor.
(3) Based on $65/Ft. static head.
(4) Based on $52.50/Ft. static head.
### Table 5-3
PROPOSED AERATORS FOR $\text{H}_2\text{S}$ REMOVAL

<table>
<thead>
<tr>
<th>Percent $\text{H}_2\text{S}$ Removed</th>
<th><strong>APOPKA</strong></th>
<th></th>
<th><strong>MAITLAND</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated Contact Time (min)$^1$</td>
<td>Selected Aerator (GPM)</td>
<td>Available Contact Time (min)$^2$</td>
<td>Calculated Contact Time (min)$^1$</td>
</tr>
<tr>
<td>10</td>
<td>0.54</td>
<td>2500</td>
<td>0.71</td>
<td>0.24</td>
</tr>
<tr>
<td>15</td>
<td>0.84</td>
<td>3500</td>
<td>1.19</td>
<td>0.37</td>
</tr>
<tr>
<td>20</td>
<td>1.15</td>
<td>3500</td>
<td>1.19</td>
<td>0.51</td>
</tr>
<tr>
<td>25</td>
<td>1.48</td>
<td>5000 (4)</td>
<td>2.02</td>
<td>0.66</td>
</tr>
<tr>
<td>30</td>
<td>1.84</td>
<td>5000 (4)</td>
<td>2.02</td>
<td>0.81</td>
</tr>
<tr>
<td>35</td>
<td>2.22</td>
<td>5000 (5)</td>
<td>2.21</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>2.63</td>
<td>5000 (7)</td>
<td>2.60</td>
<td>1.17</td>
</tr>
<tr>
<td>45</td>
<td>3.08</td>
<td>5000 (10)</td>
<td>3.17</td>
<td>1.37</td>
</tr>
<tr>
<td>50</td>
<td>3.57</td>
<td>5000 (13)</td>
<td>3.80</td>
<td>1.60</td>
</tr>
<tr>
<td>55</td>
<td>4.11</td>
<td>5000 (15)</td>
<td>4.18</td>
<td>1.83</td>
</tr>
</tbody>
</table>

(1) See table 4-4, based on existing conditions and weir overflow rate held constant @ 7.1 GPM/FT (Apopka); 13.2 GPM/FT (Maitland).

(2) Based on storage in aerator.
### Table 5-4

<table>
<thead>
<tr>
<th>H₂S Percent Removal (%)</th>
<th>Annual Aeration Costs ($)</th>
<th>Annual Chlorine Costs ($)</th>
<th>Total Annual Aeration Plus Chlorine Costs ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Appopka</td>
<td>Maitland</td>
<td>Appopka</td>
</tr>
<tr>
<td></td>
<td>($)</td>
<td>($)</td>
<td>($)</td>
</tr>
<tr>
<td>10</td>
<td>1320</td>
<td>1095</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td>1500</td>
<td>1170</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>1755</td>
<td>1755</td>
<td>65</td>
</tr>
<tr>
<td>25</td>
<td>2093</td>
<td>1755</td>
<td>60</td>
</tr>
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<td>30</td>
<td>2735</td>
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<td>35</td>
<td>4757</td>
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<td>50</td>
</tr>
<tr>
<td>40</td>
<td>5420</td>
<td>5420</td>
<td>45</td>
</tr>
</tbody>
</table>

(1) Costs reflect O&M ($30); power costs; capital costs.

(2) Costs based upon $350/ton chlorine and a 10:1 (H₂S:Cl₂) demand.
Fig. 5-3
APOPKA
ANNUAL COST EVALUATION FOR H2S REMOVAL
BY AERATION AND CHLORINATION
Percent H2S Removed by Chlorination (%)

Percent H2S Removed by Aeration (%)

Annual Cost ($1000's)

Chlorine
Aerator
Combined

Economic Range For Treatment
@ T = 20° C
Fig. 5-4
MAITLAND
ANNUAL COST EVALUATION FOR H₂S REMOVAL
BY AERATION AND CHLORINATION
Percent H₂S Removed by Chlorination

Percent H₂S Removed by Aeration

Annual Cost ($1000's)

Range For Treatment
@ T = 20° C
Several courses of action may be considered at these locations to increase the rate of \( \text{H}_2\text{S} \) removal and its ultimate effectiveness. These considerations are as follows:

1. Increase agitation in the trays, curb area and exit from the pipe riser.
2. Increase the weir overflow rate over the trays.
3. Increase the number of trays to increase the contact time.

In rating the operation at an existing location, sunk cost incurred by that existing facility should not be included in the economic evaluation.

The uniform annual costs for aerators at Apopka and Maitland are $510 and $435, respectively. When these values are subtracted from the equivalent annual costs indicated in Table 5-1, the adjusted costs are as follows:

<table>
<thead>
<tr>
<th>Annual Costs</th>
<th>Aerator</th>
<th>Chlorination</th>
<th>% H2S Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apopka</td>
<td>$810</td>
<td>$1225</td>
<td>12.92</td>
</tr>
<tr>
<td>Maitland</td>
<td>$665</td>
<td>$640</td>
<td>14.29</td>
</tr>
</tbody>
</table>

When these sunk costs have been subtracted from the annual aerator costs; and compared to the corresponding cost for chlorination to remove the same \( \text{H}_2\text{S} \) percentage, the aerator appears to be more cost effective. Apopka is considerably less expensive in annual aerator cost, whereas, Maitland is marginal.
Both chlorine gas and power costs are expected to rise in the near future. The relative rate of this cost escalation will have an impact on the treatment alternative and the optimal operational aeration range. Therefore, every effort should be provided to optimize aerator efficiency at all existing and proposed locations.

In conclusion, this study provides a means to rate existing aerator operations. From the synthetic methodology contained herein, an optimal aeration H₂S removal range can be determined. The difference between this desired H₂S removal efficiency, and the prevailing conditions, can be converted into a cost value and used in the justification of upgrading the aerator's existing operation. This cost savings generates primarily from reduced chlorination costs, since the H₂S will be released in greater amounts to the atmosphere and not in solution. And finally, although H₂S removal is the primary topic of this report, other water constituents, like iron, manganese and carbon dioxide, which also cause taste and odor problems, need to be considered in a thorough economic review of a given aeration application.
LIST OF REFERENCES


