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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

TRANSFORMATIONS OF SULFUR DIOXIDE IN WASTE STABILIZATION PONDS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

BILLY SHELTON SMITH

Oklahoma City, Oklahoma

1972

TRANSFORMATIONS OF SULFUR DIOXIDE

IN WASTE STABILIZATION PONDS

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LIST OF ABBREVIATIONS

a - acre(s)

cc - cubic centimeters

cf - cubic feet

cf/d/lb - cubic feet per day per pound

cfh - cubic feet per hour

cfm - cubic feet per minute

d - day

deg - degrees

eff - effluent

ft - feet

ft-c - foot candles

gal - gallons

in - inch(es)

inf - influent

lb - pounds

lb/a/d - pounds per acre per day

lb/d - pound per day

lpm - liters per minute

mg/l - milligrams per liter

ml - milliliters

ppm - parts per million

sq in - square inches

w - watts

°C - degrees centigrade

°F - degrees Fahrenheit

TRANSFORMATIONS OF SULFUR DIOXIDE IN WASTE STABILIZATION PONDS

CHAPTER I

INTRODUCTION

Although man has achieved a high degree of sophistication in technological and sociological developments in the past half century, he has not fully developed and applied the means necessary to assure him of a safe and healthful physical environment. Environmental problems have existed throughout history, yet they have not always been a central topic seriously discussed by a large segment of society. Rather, they have crept along and accumulated in the wake of industrialization and scientific advancements. For example, chemical methods for controlling pests have been an integral part of agriculture for more than 25 years, but during most of this period there was either a lack of knowledge, understanding or willingness to recognize the potential dangers to the environment of excessive use or misuse of pesticides. The rising concern about the environment, however, has changed the traditional concept of what is desirable. Increased production alone of any goods or service without regard to effects on the environment has become unacceptable. Until recent years the selection of a fuel for conversion to electrical energy was simply based on the lowest overall cost with little emphasis

on its effects on the environment. The effects of production, processing and utilization of each of the principal energy sources such as coal, oil, gas, hydro and nuclear, all of which have differing environmental effects, must now be carefully considered.

The environmental aspects of modern science appear to lag far behind the technological aspects. A wide variety of new chemicals have been synthesized at a relatively high rate for various applications, but often without the concurrent publication, or knowledge, of acute and chronic toxicity data to plants and animals or the long-term effects on the eco-system. The state of knowledge of the effects of pollutants on the aggregate of living things as they exist in nature seems primitive.

In this era of expanding industrialization and increasing population, control of environmental pollution has become recognized by many as a crucial challenge with possibly the survival of mankind at stake. The well publicized and tragic air pollution episodes such as occurred in Donora, Pennsylvania and London, England resulted in impairment to human health as well as the loss of plant and animal life. Large bodies of water have been polluted by accidental spills of crude oil which may have unbalanced the eco-system in some cases. The occurrence of such disasters should serve as a forewarning of what could possibly happen on a much larger scale if the dangers of continuing to pollute the environment are not soon recognized and controlled.

The relatively recent concern and recognition that the environment is indeed a finite medium and a place in which to live and not a sink for massive, complex waste products has provided the motivation to explore methods of either preventing pollution or possibly assimilating

wastes back into the environment as useful products. On the national level the Environmental Protection Agency (EPA) was established to deal with pollution problems in a number of areas including air, water and solid waste pollution. One of the primary aims of the EPA was to achieve an interrelated approach to the environment; to treat the problems in a systematic way rather than assuming, for example, that solutions to solid waste problems could be obtained without considering possible effects to other aspects of the environment. Certainly it is not acceptable to water scrub an air pollution problem only to create stream pollution or to burn solid waste only to create air pollution. Bregman (1) appropriately stated that: "Today everyone lives in someone else's backyard, everyone lives down wind or down stream from someone else. We can no longer throw our wastes away carelessly and expect them to harm no one." The best efforts of many people from a variety of disciplines are needed in order to restore and protect the vital resources of air, water and earth. The environmental system is by nature geopolitical, but pollutants have no national or international boundaries, and the approach to solutions of almost infinitely complex management and control problems must involve not only the best efforts from those in the scientific community, but coordination with other disciplines such as law, sociology, politics and economics.

Efficient management of air and water pollutants not controlled at the source, must eventually depend on a thorough knowledge of how pollutants flow, disperse and are degraded or converted into other physical and chemical forms as they move from source to sink.

The reactions of sulfur compounds, especially sulfur oxides, in

the atmosphere and water have recently received considerable attention, but the complex nature of a polluted atmosphere or body of water is such that it has been extremely difficult to measure and understand chemical interactions. Most studies of atmospheric interactions of sulfur oxides have been conducted under controlled laboratory conditions which were not usually representative of a complex polluted matrix. The pattern of flow and dispersion of sulfur in nature is shown in Figure 1.

At present the major source of sulfur dioxide (SO_2) emissions, illustrated in Figure 2, is combustion of coal (2). The pungent odor of SO_2 and its adverse effects on health have been known and recorded for many centuries. For example, it has been proposed that the death of Pliny the Elder, scholar and writer, was partially due to sulfurous fumes inhaled while he was aiding refugees and observing the eruption of Vesuvius in A.D. 79 (3). In more recent years several investigators have examined the response of humans, laboratory animals and plants to known concentrations of SO_2 (4). Some disagreements have been reported regarding the levels of pollutants in the atmosphere which impair health. This has been partly due to a lack of fundamental knowledge of reaction mechanisms, methods of obtaining and analyzing data, deficiencies in analytical methods employed, and the lack of understanding of the interplay between the individual and the stresses of his external environment. The problems of applying dose-response relationships for SO_2 to the etiology of certain pulmonary impairments have been further complicated by the potentiating and synergistic effects of a number of substances, especially particulate matter and trace metals, found along with sulfur oxides in a polluted atmosphere (5).

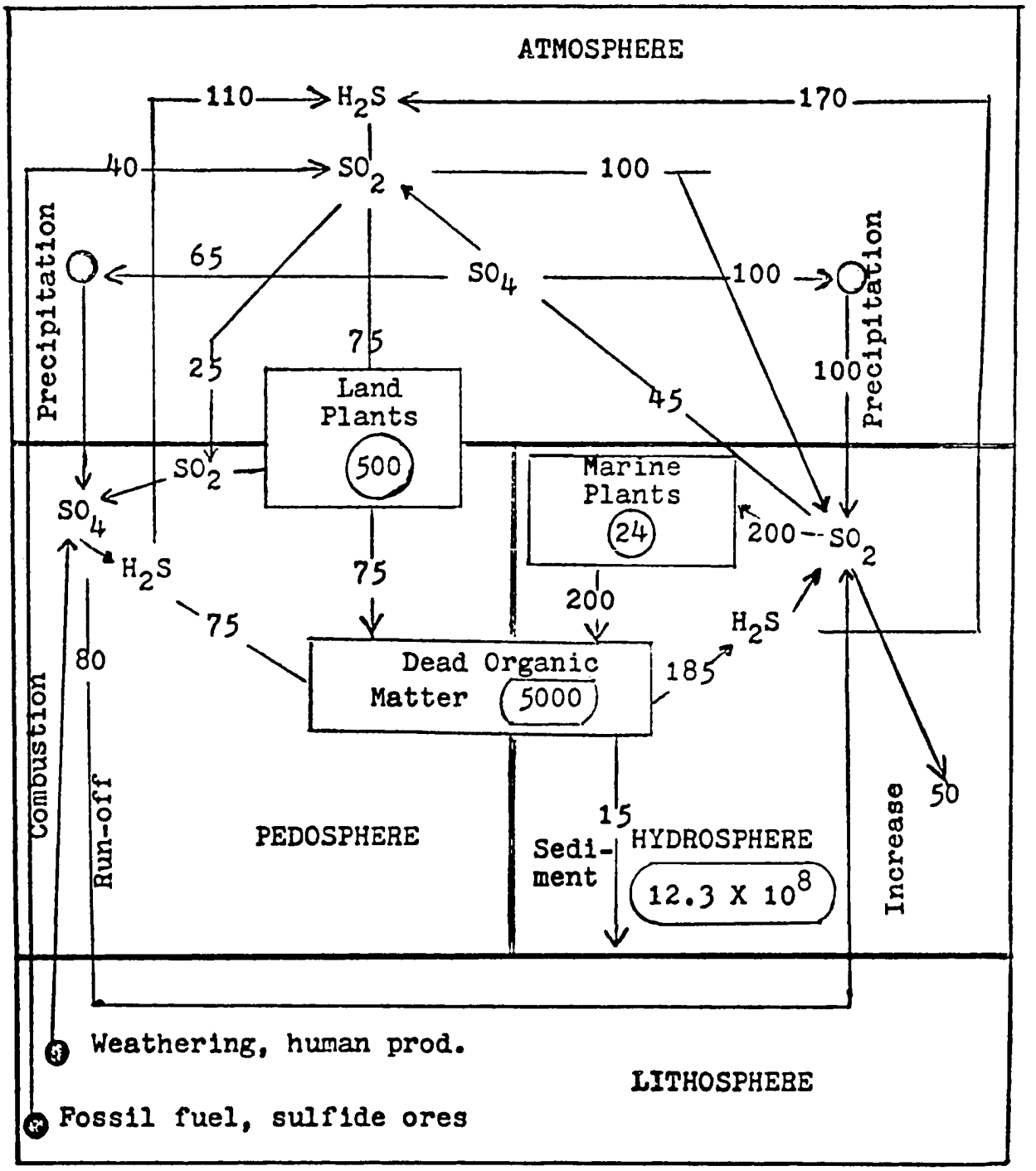

Figure 1--Circulation pattern of sulfur in nature and estimated fluxes. Circled numbers are amounts present in different reservoirs; other numbers are yearly fluxes, all in million tons of sulfur units (2).

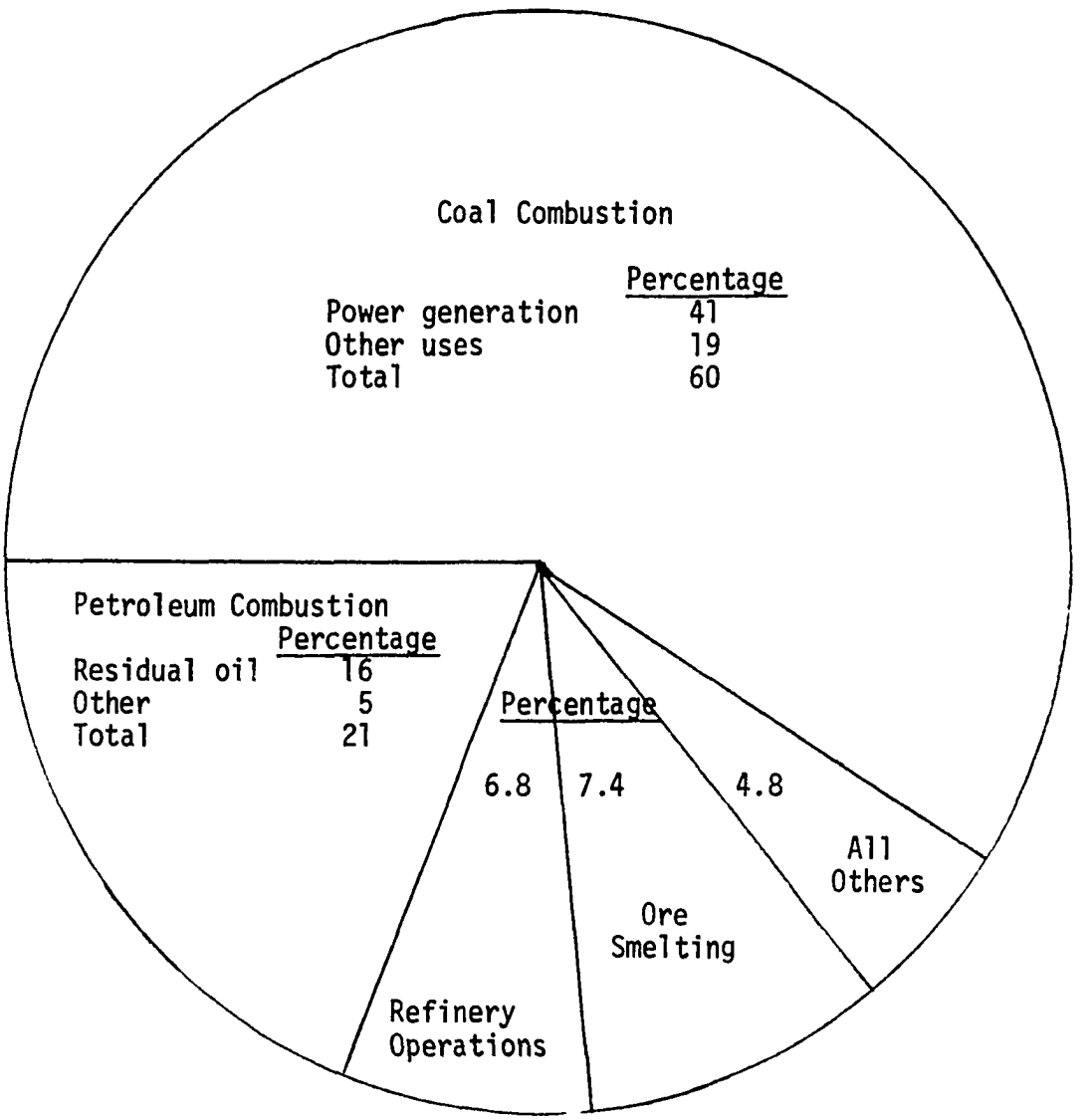

Figure 2--Major sources of sulfur dioxide (2).

A number of approaches to reduce the amount of sulfur oxides entering the atmosphere have been proposed and investigated in recent years (6). Fuel switching, desulfurization of coal and residual fuel oil, and flue gas treatment are the primary categories under which much of the research has been conducted. The possibilities of combining the treatment of a specific air pollution problem such as SO_2 with conventional liquid-carried waste treatment methods have not been investigated in detail.

One of the more recent methods of treating domestic and industrial liquid-carried wastes involves utilizing part of nature's biological resources to oxidize waste products in waste stabilization ponds (WSP). The history of this treatment process dates back several centuries; however, only during the past 50 years has it been studied and developed extensively as a modern treatment method. The WSP method of treating liquid-carried wastes now ranks as a major waste treatment system (7). The term "stabilization pond" has been commonly used to describe those bodies of water specifically created for the purpose of impounding aqueous organic wastes to be decomposed by microbes with subsequent disposition of the water back to the environment either through evaporation, seepage or by discharge into water receiving courses (8). Other terms which have sometimes been used interchangeably to describe essentially the same process are "oxidation ponds" and "lagoons".

The basic advantages of the WSP method of waste treatment over the more conventional methods include: (9)

a) relatively low operating and capital cost

b) low operating skill requirements

c) relatively resistant to upsets

d) obtain a high-quality effluent

e) ability to treat high-strength and variable wastes

The very low operating and capital cost factor has been most pronounced in rural areas or other locations where the price of land was not excessive.

In the different types of ponds, waste materials to be treated are placed in contact with an active microbiological population consisting mainly of algae and bacteria acting in a mutually beneficial manner to decompose or stabilize the waste. During the stabilization processes organic matter is sequentially and continuously converted to simpler intermediate and end products with a simultaneous synthesis of a biomass.

The specific mechanisms by which the various members of the biological population assimilate and dissimilate particular classes of chemical substances such as those compounds containing phosphorous and sulfur are not thoroughly understood. Oswald (10) stated that: "The complexity of actions and interactions in ponds has been great enough to deter scientific investigations and there has been a tendency to utilize empirical designs having only a superficial basis and doubtful benefits." Part of the difficulty in establishing the nature of chemical reactions in ponds is associated with the variable and highly complex composition of wastes introduced into ponds (11).

Stabilization ponds have been used to treat domestic wastes in different geographical areas and to treat a large variety of agricultural and industrial wastes. The spectrum of application of ponds also includes treatment of wastes associated with the pulp and paper industry,

abattoir wastes and petroleum refinery wastes (12, 13). Wastes from these operations often contain a very high biochemical oxygen demand (BOD) in addition to large quantities of organic and inorganic sulfur compounds.

Another application for the WSP was recently suggested by Hobson et al. (14) in which a WSP was used to scrub SO_2 from an air stream. They demonstrated the possibility of combining an air pollution control problem and a liquid-carried waste treatment method into a single environmental control system. The WSP, which commonly operates under relatively high alkaline conditions, was found to be an efficient scrubbing media for SO_2. This novel concept of biological treatment of air pollutants implies a number of potential benefits in the field of environmental control such as the possible production of valuable commercial by-products, incorporation of the waste into the life cycle to ultimately benefit higher plant and animal life, and become a more economical control system than separate control measures.

However, before the benefits of this combined control system can be realized, it is necessary to have a better understanding of the chemical and biological changes that occur in the ponds, and ascertain that the ponds will, in fact, continue to perform satisfactorily on a long term basis while receiving high concentrations of SO_2. The chemical interactions and fate of the sulfur incorporated into the pond along with the effect of adding other stack gases, such as carbon dioxide, to be scrubbed have not been investigated. Another area which merits study, is the use of a double-cell pond designed such that the second cell receives the neutralized effluent from the scrubbing pond.

CHAPTER II

LITERATURE REVIEW

Sulfur Dioxide

The majority of the SO_2 found in polluted atmospheres over metropolitan areas has been the result of combustion of sulfur-bearing fuels. In 1966 an estimated 28.6 million tons of SO_2 were emitted into the atmosphere in the United States (6). Approximately two pounds of SO_2 are produced from each pound of sulfur contained in coal or residual fuel oil. Figure 3 shows the potential tonnage of SO_2 that could occur in the atmosphere with the passage of time if no air pollution control measures were applied (6). The potential increase in SO_2 emission is derived from a projected increase in fossil fuel consumption. The tapering off of SO_2 emission in about the year 1990 is due to an expected increase in nuclear power plants to replace conventional fuel burning plants. Sulfur trioxide (SO_3) is also produced during the combustion of sulfur-containing fuels but with a much lower yield than SO_2. The acids and salts corresponding to SO_2 and SO_3 have been identified as atmospheric pollutants.

Physical and Chemical Properties

Some of the physical properties of SO_2 are summarized in Table 1 (4). Sulfur dioxide is a colorless, nonflammable, nonexplosive

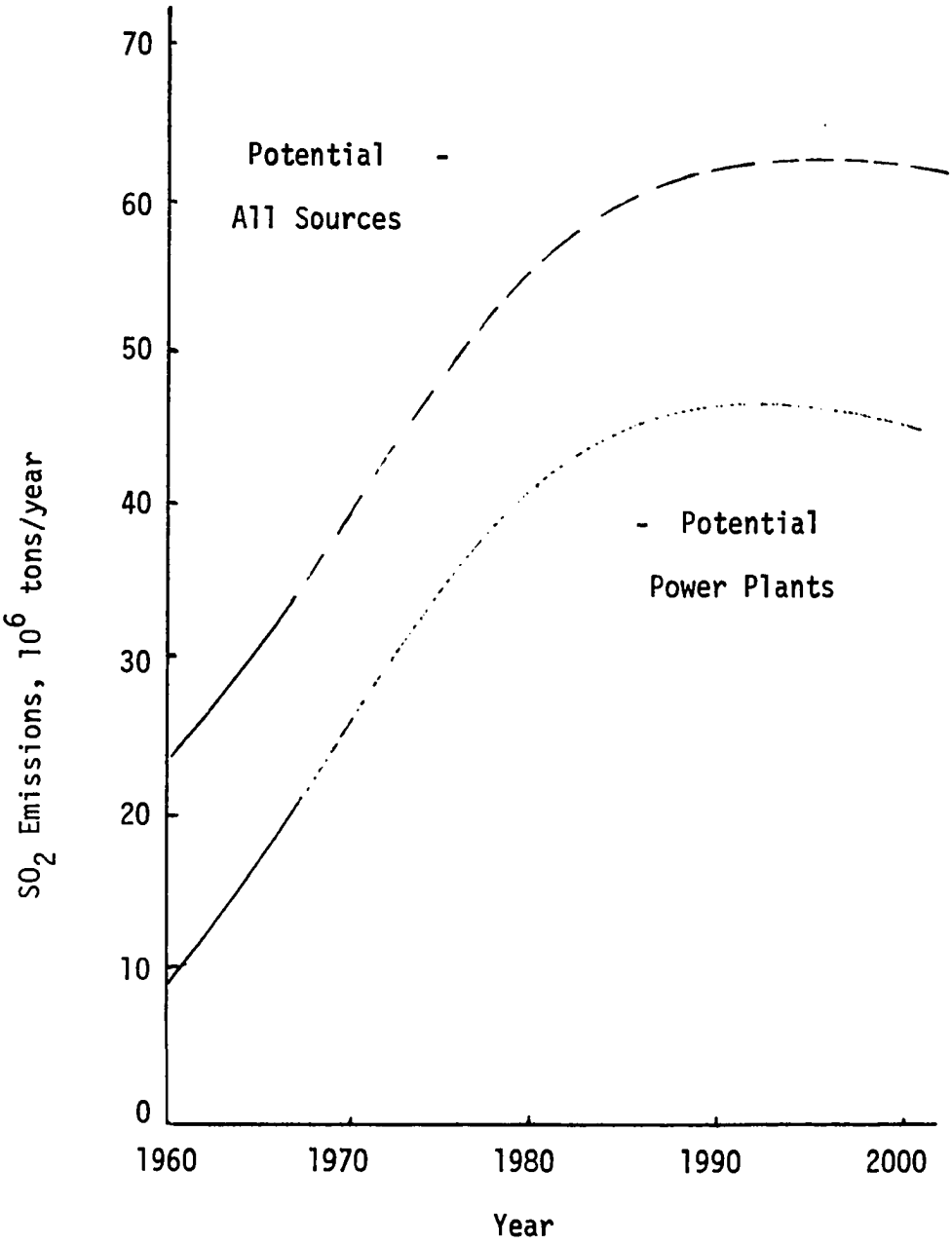

Figure 3--Estimated SO_2 emissions (6).

TABLE 1

PHYSICAL PROPERTIES OF SULFUR DIOXIDE

Molecular weight	64.06
Density (gas) g/liter	2.927 at 0°C; 1 atm
Specific (liquid) gravity	1.434 at -10°C.
Molecular volume (liquid), ml	44
Melting point, °C.	-75.46
Boiling point, °C.	-10.02
Critical temperature, °C.	157.2
Critical pressure, atm	77.7
Heat of fusion, Kcal/mole	1.769
Heat of vaporization, Kcal/mole	5.96
Dielectric constant (practical units)	13.8 at 14.5°C.
Viscosity, dyne sec/cm^2	0.0039 at 0°C.
Molecular boiling point constant, °C/1000g	1.45
Dipole moment, Debye units	1.61

gas which, according to McCord and Witheridge (15), has a pungent, irritating odor in concentrations above about 3 ppm ($8mg/m^3$). Only a limited amount of work has been published on the absorption of SO_2 in water (16); however SO_2 is highly soluble in water as shown by the solubility curve in Figure 4 from data reported by Bienstock et al. (17).

A solution of SO_2 in water gives rise to an increase in hydrogen-ion concentration, and the resulting solution is known as "sulfurous acid", H_2SO_3. Falk and Giguere (18) were unsuccessful in their attempts to detect H_2SO_3 molecules in aqueous solutions using infrared spectrometry. They found absorption bands corresponding to essentially unchanged SO_2 molecules. Cotton and Wilkinson (19) also reported that modern physical methods of study have shown that H_2SO_3 is either not present or present only in infinitesimal quantities in solutions of SO_2. They indicate that the equilibria in aqueous solutions of SO_2 are represented as:

$$SO_2 + xH_2O = SO_2 \cdot xH_2O \text{ (hydrated } SO_2\text{)}$$

$$SO_2 \cdot xH_2O = H_2SO_3 \ (K <<< 1)$$

$$SO_2 \cdot xH_2O = HSO_3^- (aq) + H_3O^+ + (x-2)\ H_2O$$

The over-all equilibrium may be represented by the following (19):

$$SO_2 + 2\ H_2O \rightleftharpoons HSO_3^- + H_3O^+$$

The first acid dissociation constant for the "sulfurous acid" is defined as (19):

$$K_1 = \frac{[HSO_3^-]\ [H^+]}{[\text{Total dissolved } SO_2] - [HSO_3^-] - [SO_3^{2-}]} = 1.3 \times 10^{-2}$$

According to Durrant and Durrant (20) SO_2 disproportionates as

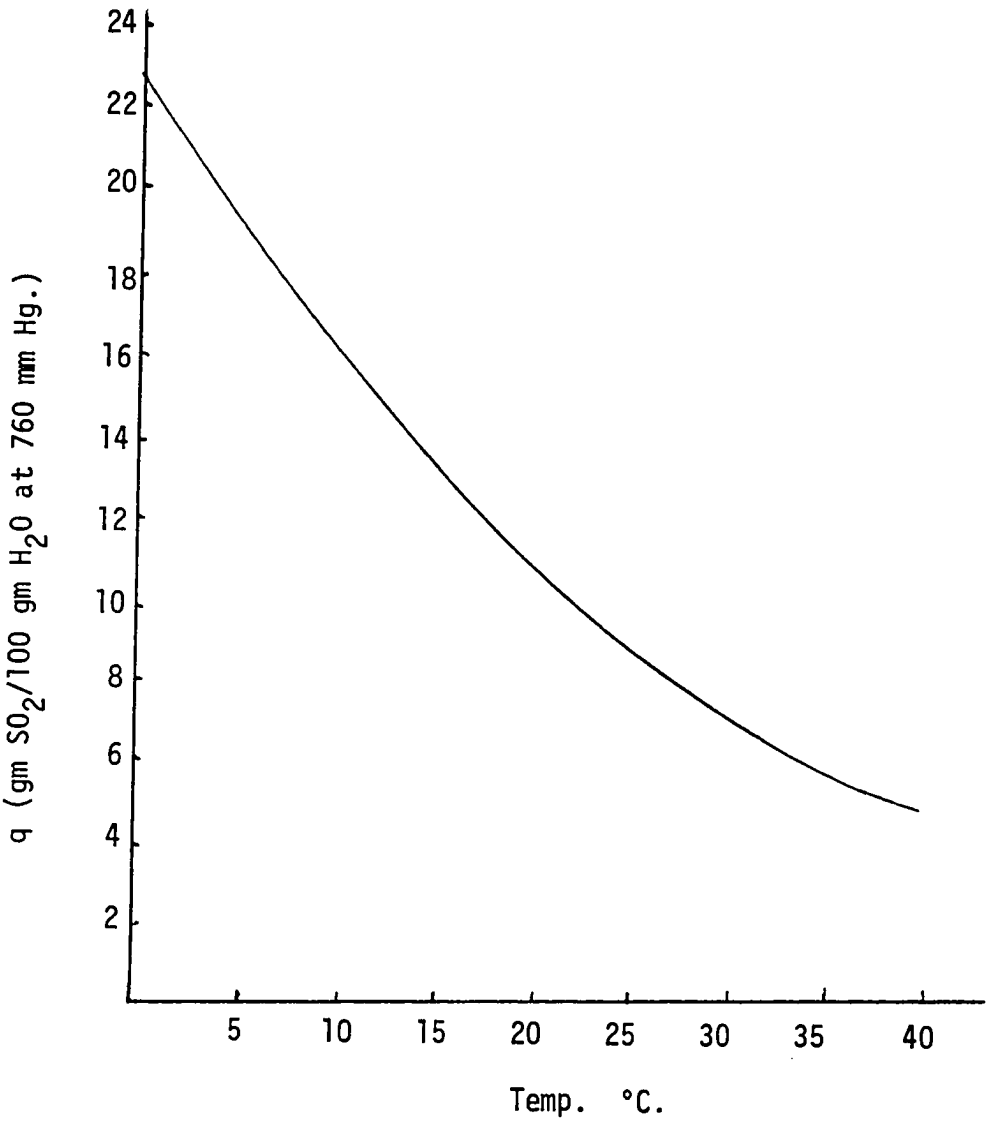

Figure 4--Solubility of SO_2 in water (17).

follows if heated with water in the absence of air:

$$2SO_2 + SO_2 = S + 2SO_3$$

$$2SO_3 + 2\ H_2O = 2H_2SO_4$$

The enthalpy of formation ($\Delta\ \overline{H}_f$) of H_2SO_4 as reported by Daniels and Alberty (21) is -193.91 Kcal mole $^{-1}$. The enthalpy of formation of H_2SO_4 is the sum of the enthalpy changes of each reaction step, such as:

$S + O_2 = SO_2$	ΔH = -70.96 Kcal
$SO_2 + 1/2\ O_2 + Pt = SO_3$	ΔH = -23.49 Kcal
$SO_3 + H_2O = H_2SO_4$	ΔH = -31.14 Kcal
$H_2 + 1/2\ O_2 = H_2O$	ΔH = -68.32 Kcal
$S + 2\ O_2 + H_2 = H_2SO_4$	$\Delta \overline{H}_f$ = -193.91 Kcal

The heat evolved from the reactions shown above indicates that the transitions are spontaneous. However, it is noted that the oxidation of SO_2 to SO_3 is enhanced by the presence of a catalyst. A number of other catalysts have been reported for the oxidation of SO_2 to SO_3 (17, 22, 23). Johnstone (23) reported an experiment in which sulfuric acid and ferrous sulfate were formed simultaneously when a mixture of air containing less than 3 per cent SO_2 was passed into a solution containing ferrous sulfate.

Bufalini (24) reviewed the photochemical reactions of SO_2 with special emphasis on the wavelength range 3,000 to 4,000 A. The influence of foreign particles and reactions of SO_2 with metal salt solutions were included. He described the work credited to Matteson in which the kinetics of the oxidation of SO_2 in aqueous aerosols of manganese sulfate

were investigated. The reaction showed the possible formation of H_2SO_4 from the interactions of SO_2, O_2, H_2O and manganese ions.

Effects of SO_2

The effects of SO_2 on man and the environment have been investigated by many people (25, 26, 27, 28). The document "Air Quality Criteria for Sulfur Oxides" (4) purportedly summarizes the state-of-the-art of the obvious and insidious effects of air pollution on man and his environment. The basis for assigning numbers to the level of pollutant necessary to protect the public health and welfare then is a collection and analysis of experimental data on man, animals, plants, and materials. In the summary to the chapter on the toxicological effects of sulfur oxides on man, one of the conclusions was that man does respond to SO_2 by bronchoconstriction assessed in terms of slight airway resistance. Amdur (5) indicated that although SO_2 alone is a mild irritant in low concentrations, when considered in conjunction with particulates such as salts of manganese, ferrous iron, and vanadium, a three- or four-fold potentiation of irritant was observed. Battigelli (29) however, in his review of health effects due to SO_2, indicated that SO_2 did not appear to be involved in the measureable effects on the health of those exposed to urban pollution.

Daines (30) cited papers in his review of the effects that SO_2 had on vegetation including conifers, cotton, alfalfa, potatoes, tomatoes and other plants. Many plants were reported to respond to SO_2 concentrations of about 0.5 to 0.6 ppm.

Removal of SO_2 from Stack Gases

Bienstock et al. (17) in a detailed summary of the chemistry of SO_2 and its removal from waste gases, included a process description and schematic of the London Power Company's Battersea Power Station. This process which has been in operation since 1935 uses Thames River water, to which a small quantity of chalk is added, to scrub SO_2 from the stack gas. The process required some 35 tons of water per ton of 1.0 per cent sulfur-bearing coal. The reaction of the SO_2 with the alkaline slurry, which was added to the river water that contained considerable calcium bicarbonate alkalinity, produced calcium sulfate. The efficiency of this process was reported to be about 92 to 97 per cent. The main difficulties of this method were the high cost of maintenance, extent to which the process cooled the stack gases, the strict limitation on the sites at which the operation could be employed, and the amount of water required for scrubbing the stack gases.

Current methods of removing SO_2 from stack gases were reviewed by Reid (31) and Hangebrauck and Spaite (32). One of the methods discussed was the limestone-dolomite process which uses the chemical either by injecting them dry directly into the furnace or in solution to scrub the stack gases. A combination of the wet and dry processes may also be used. The efficiencies of these methods for removing SO_2 range from 83 to 91 per cent. If a stack produces 1,000 ppm SO_2, removal of 90 per cent leaves an emission of at least 100 ppm and the problem would not be solved.

A discussion of the Bureau of Mines proposed alkalized alumina process was also included in the paper by Reid (31). In this process

gases rich in SO_2 were passed over a bed of alkalized alumina which absorbed and oxidized the SO_2 to sulfate. The alkalized alumina was regenerated by stripping off the sulfur with hydrogen to yield H_2S from which elemental sulfur was recovered.

Many other processes were discussed in this same paper, including catalytic oxidation and adsorption of SO_2 onto activated charcoal. Most of the processes for removing SO_2 from stack gases fail to be economically feasible. As emission standards for SO_2 have become more strict, the cost of removal for the last few per cent has increased. This means increased expense for production and higher prices for the consumer.

The above discussion indicates that SO_2 has been of public concern when damage to plants, animals, material and man were involved, and that this concern has resulted in considerable effort to find new or different control measures through fundamental research on the behavior of SO_2 in the environment. One such control measure involves a unique application of a domestic waste treatment process.

Waste Stabilization Ponds

This method of treating liquid-carried wastes has been practiced extensively for many years. Improvements in design and other modifications, especially subsurface aeration, have allowed for sizeable increase in loading rates and shortened detention time thus permitting the use of smaller land areas to treat wastes (33). The Hinde Engineering Company (34, 35) reported a subsurface aeration system in which compressed air was vented through perforated plastic pipes installed at regular intervals on the bottom of the WSP. The pond depths for this system ranged from 10 to 12 feet of water with a loading rate ranging from 1,000 to

1,300 persons per acre and air requirements of about 700 cf/d/lb of BOD. The typical nonaerated WSP was reported to operate at a loading rate of about 200 persons per acre and average depth of 4 feet (36).

The degradation of sewage organic matter in the WSP in the presence of dissolved oxygen has been described by Oswald et al. (37), Varma et al. (38), Nemerow (39) and Eckenfelder and O'Connor (40) as follows:

$$C_{11}H_{29}O_7N + 14O_2 + H^+ \rightarrow 11\ CO_2 + 13H_2O + NH_4^+$$

$$6(CH_2O)_x + 5\ O_2 \rightarrow (CH_2O)_x + 5CO_2 + 5H_2O + \text{energy}$$

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

According to Eckenfelder and O'Connor (40), the weight of oxygen required to oxidize organic matter is 1.56 times the BOD entering the pond.

The production of CO_2 from the decomposition of organic matter tends to lower the pH; however, algae production (photosynthesis) consumes the CO_2 and was reported to cause the pH in the pond to rise (7, 41). According to Pipes (41) the rate of CO_2 consumption by algae during the day time exceeded the CO_2 production by decomposition of organic matter and caused a shift in the carbonate and bicarbonate system of the pond which may be illustrated as follows:

$$2HCO_3^- \rightleftharpoons CO_2 + CO_3^= + 2H_2O$$

or $$HCO_3^- \rightleftharpoons CO_2 + OH^-$$

As the concentration of the bicarbonate decreases there is an equivalent increase in the concentration of $CO_3^=$ or OH^- resulting in no change in total alkalinity of the water. The reaction according to Pipes (41) is represented below as:

$$CO_3^{=} + H_2O \longrightarrow CO_2 + 2\ OH^-$$

Canter (42) indicated that the process was as follows:

$$HCO_3^- \longrightarrow CO_2 + OH^-$$

The pH, according to this, may increase and reach to 10 or 11 during the day.

Other investigators have reported that certain bacteria inhabiting ponds have the ability to produce alkaline reactions (43). Malek and Rizk (44) showed that high alkalinity developed during sulfate reduction and the final pH in a number of experiments ranged between 8.6 and 8.8 irrespective of the initial pH of the media.

The pH of the water in the WSP controls the availability or withdrawal of protons and consequently influences the reversibility of oxidation-reduction reactions indicated by the following equations in which (S) is an organic substrate (45):

$$(S)H^+ + 2H_2O \longrightarrow (S)HOH + H_3O^+ \quad \text{(oxidation)}$$

$$(S)H^- + H_3O \longrightarrow (S)H_2 + H_2) \quad \text{(reduction)}$$

Goltschaldt (46) has suggested that it is difficult to measure and interpret real redox potentials in highly complex multicomponent systems such as the heterogeneous biological system represented by waste water treatment processes. Pohland (45) however, indicated that such measurements are useful indicators for process conditions and stabilization efficiency in spite of the difficulty in providing rigorous and definitive conceptual interpretations. pH values ranging from approximately 6.5 to 8.7 are generally thought to be optimum for most biological activity, and pH values in extremes of this in WSP results in

decreased efficiency of BOD removal (41). Cooke (47), Harvey (48) and Lackey (49) have reported the role of fungi, organisms capable of tolerating low pH, in acid mine drainage and stabilization of organic wastes.

The occurrence and interactions of sulfur compounds in waste treatment methods have rarely been reported in the literature. Starkey (50) has appropriately stated that: "Considering the great diversity of organic sulfur compounds in plants and animals and their metabolic importance, it is surprising that there is relatively little information on the dissimilation of these compounds, on the microorganisms concerned in the transformation, and on the sulfur products formed." A schematic description of the primary biological transformations of sulfur in nature is shown in Figure 5. Hobson et al. (14) summarized the microbial transformations of sulfur as follows:

1. When the sulfur compound becomes part of the cell there is:
   a) synthesis of sulfur-containing amino acids
   b) synthesis of sulfur-containing organic co-factors.
2. When the sulfur compound does not become part of the cell the sulfur compound becomes:
   a) a hydrogen acceptor
   b) a hydrogen donor, and the carbon dioxide (and/or) molecular oxygen becomes the hydrogen acceptor.

It is believed that the majority of the sulfur interactions are controlled by reactions according to (2) above, and hence exists in solution rather than in the biomass or as free elemental sulfur.

The major groups of microorganisms involved in sulfur transformations have been reported by several authors (44, 50, 51, 52, 53, 54).

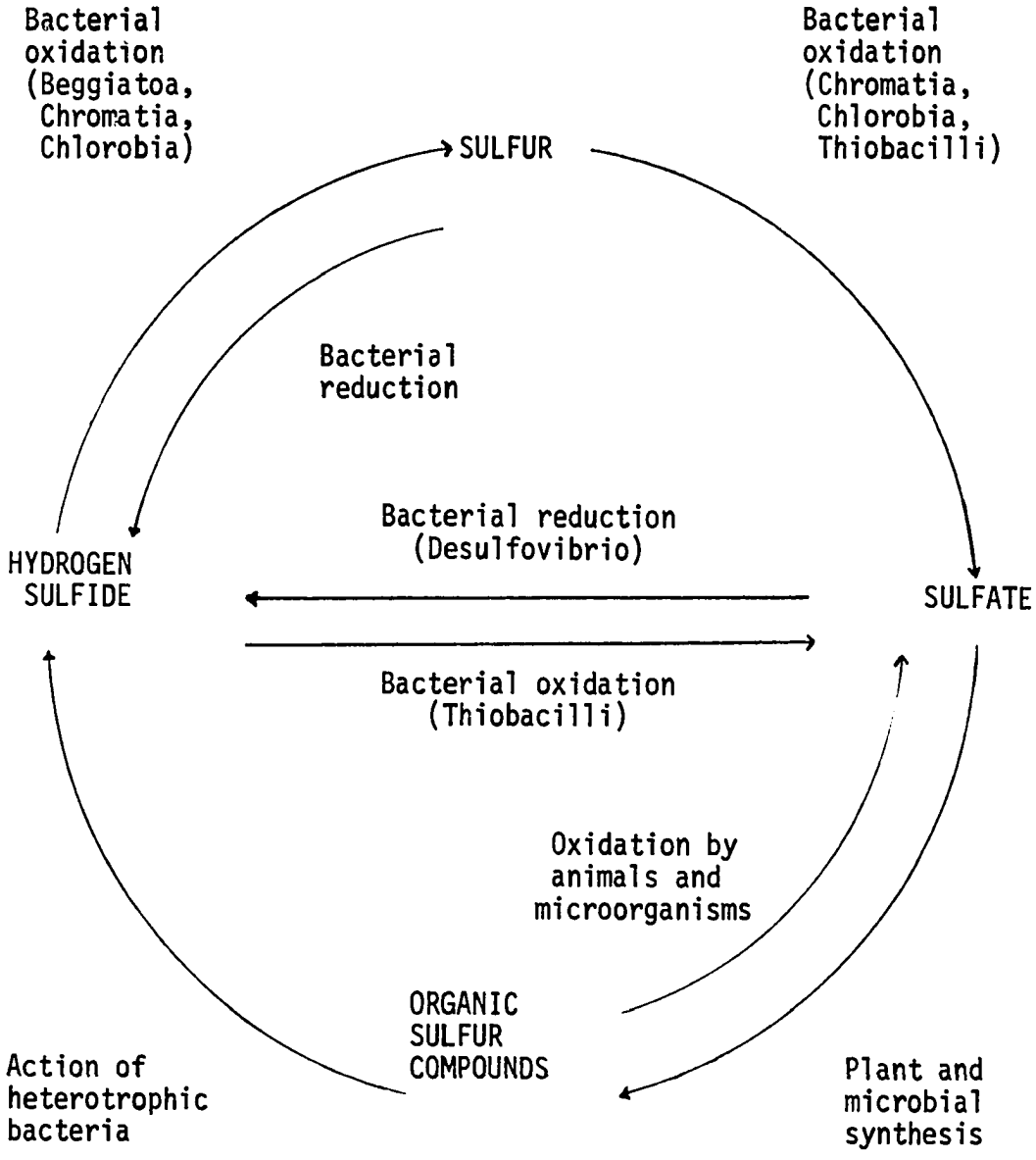

Figure 5--Sulfur transformations (51).

Postgate (54), considered one of the authorities on sulfate reducing bacteria, outlined the detailed mechanisms of sulfate reduction by the Desulfovibrio species. Gloyna and Espino (53) investigated sulfide production in a WSP with respect to sulfate concentrations. They reported the disappearance of algal growth at sulfide concentrations of 6.5 to 8.5 mg/l which occurred at a sulfate concentration of 400 mg/l. The effect of pH on hydrogen sulfide-sulfide equilibrium is shown in Figure 6.

Burgess and Scott (55, 56, 57, 58) reported on a project to the London County Council, England, in which elemental sulfur was recovered from sulfide gases produced in a pilot plant sludge digestion tank. Calcium sulfate was added to the sludge tank as a source of sulfur.

In summary, the versatility and advantages of the WSP and several known and postulated reactions that occur in the pond environment, along with the chemical and physical properties of SO_2, have been pointed out. The alkaline conditions under which the WSP frequently operate, the buffering capacity and presence of a great variety of ions in the domestic sewage feed, and the ability of fungi and other microorganisms to adapt and degrade organic wastes are among the features encountered in a WSP which make it a potentially suitable media for scrubbing SO_2 from an air stream. However it has not been shown that a pond receiving high concentrations of SO_2 will continue to function over an extended period of time. The low pH resulting from the addition of SO_2 could severely limit microbiological activity. The transformations of the SO_2 into other sulfur compounds have not been investigated to determine if more or less toxic sulfur compounds are produced. These areas must be investigated before practical application can be made of this environmental control method.

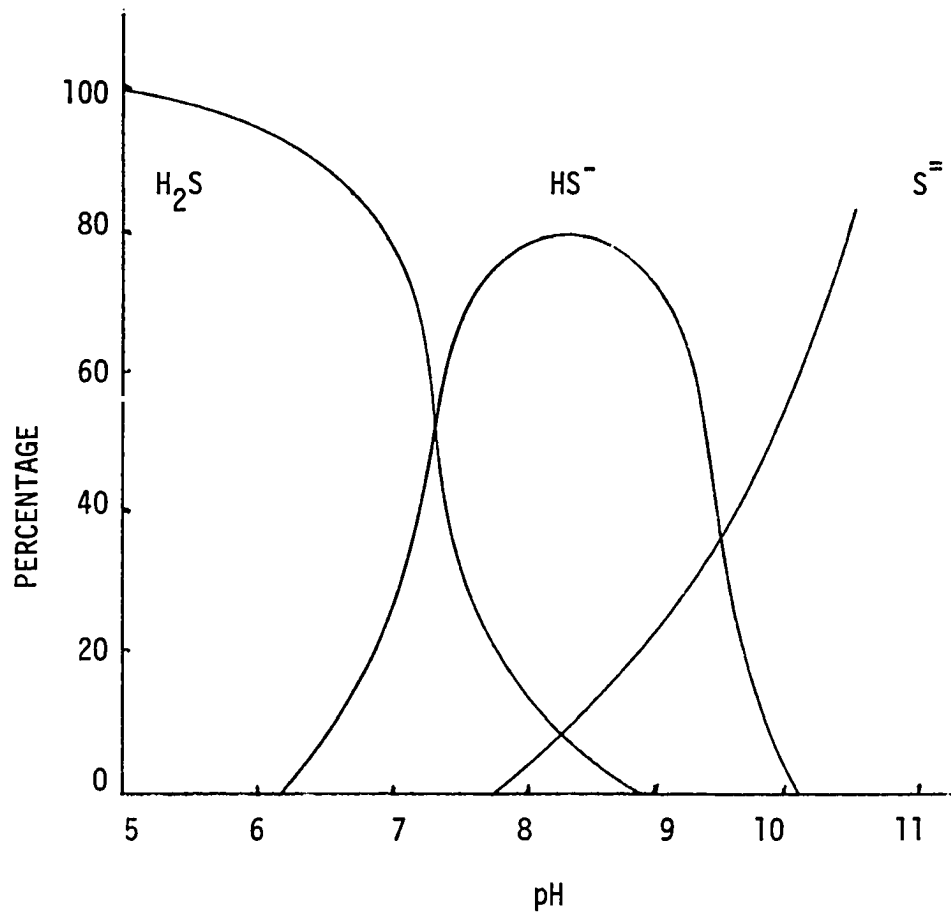

Figure 6--Effect of pH on hydrogen sulfide-sulfide equilibrium (10^{-3} molar solution, 32 mg H_2S/l) (59).

CHAPTER III

PURPOSE AND SCOPE

It has been previously demonstrated by Hobson et al. (14) that waste stabilization ponds may be used to scrub a relatively high concentration of SO_2 from an air stream and still yield satisfactory performance in BOD reduction. Their investigation introduced the concept of incorporating the treatment of an air pollution problem into a treatment method for liquid-carried waste and the formation of a combined environmental control system. However, their study involved the evaluation of pond scrubbing efficiencies and performance on a short term basis, and did not consider mechanism of SO_2 removal nor the role and fate of the sulfur entrained in the pond. The latter considerations will ultimately control the practicality and applicability of the process.

The purpose of this study was to investigate the mechanism of transformation and nature and distribution of sulfur compounds formed after SO_2 was scrubbed from an air stream into waste stabilization ponds; to observe WSP performance over an extended period of time; to determine equilibrium conditions and to determine the effect of adding a second stack gas, carbon dioxide (CO_2), to the air stream containing SO_2.

Specifically, the scope of the project was to operate six laboratory aquaria, five of which received raw domestic sewage at a rate of approximately 150 lb/a/d BOD at a hydraulic loading of 8 liters per day

for an approximate 4-day retention time. One of the five WSP was aerated with air only at approximately 1 lpm and served as a control pond. A second pond received air and 1,000 ppm (2623 mg/m^3) SO_2 at a rate of 1 lpm. Carbon dioxide was added to the SO_2 and air stream at the rate of 100 cc/l of air-SO_2 and metered into the third pond. The fourth and fifth ponds received a mixture of 1,000 ppm SO_2 and 5 per cent CO_2 at 1 lpm. In order to simulate the effects of hot stack gases, the fifth pond was heated to approximately 40° C. A nonaerated sixth pond was used to receive only neutralized effluent from pond three, thus forming essentially a two-cell operation with WSP-3 functioning as the SO_2 scrubbing unit and WSP-6 functioning as a polishing pond.

Observations were made for dissolved SO_2, sulfide ($S^=$), sulfite ($SO_3^=$) and sulfate ($SO_4^=$) ions in the ponds. The long term effects on waste treatment were evaluated by observing and comparing the BOD reduction values and nitrogen reduction values against the control pond. The pH and temperature of the ponds were also monitored.

CHAPTER IV

MATERIALS AND PROCEDURES

Four of the experimental laboratory WSP used during this investigation had been used for previous projects (14, 33). Figure 7 shows the ponds as they were physically arranged for this study. The ponds were made of 10-gal glass aquaria with a surface area of 200 sq in and a liquid depth of approximately 10 in.

Each aquarium was lighted by a bank of five 15-w Sylvania Gro-Lux fluorescent light bulbs positioned 12 in above the liquid level to produce an intensity of 350 ft-c at the surface of the ponds. A 12-hour-on, 12-hour-off light cycle was provided by two Intermatic timer switches. A 150-w General Electric infrared light bulb was placed against the side of WSP-5 to increase the pond temperature to approximately 40° C.

Two of the five ponds were aerated with fritted glass type aerators positioned 6 in below the liquid surface. Three of the other ponds were aerated with diffusers, shown in Figure 8, designed by Hobson (33) from four lengths of 0.5-in diameter PVC plastic, 26-g needles and 1-cc tuberculin syringes. The aerators were placed in the pond so that the bubbles originated approximately 6 in below the surface of the liquid. Each bubbler in the diffuser consisted of a 26-g needle attached to the last inch of a tuberculin syringe barrel cemented into the PVC tubing at approximately 45 deg and placed every 2 in on the outside lengths and

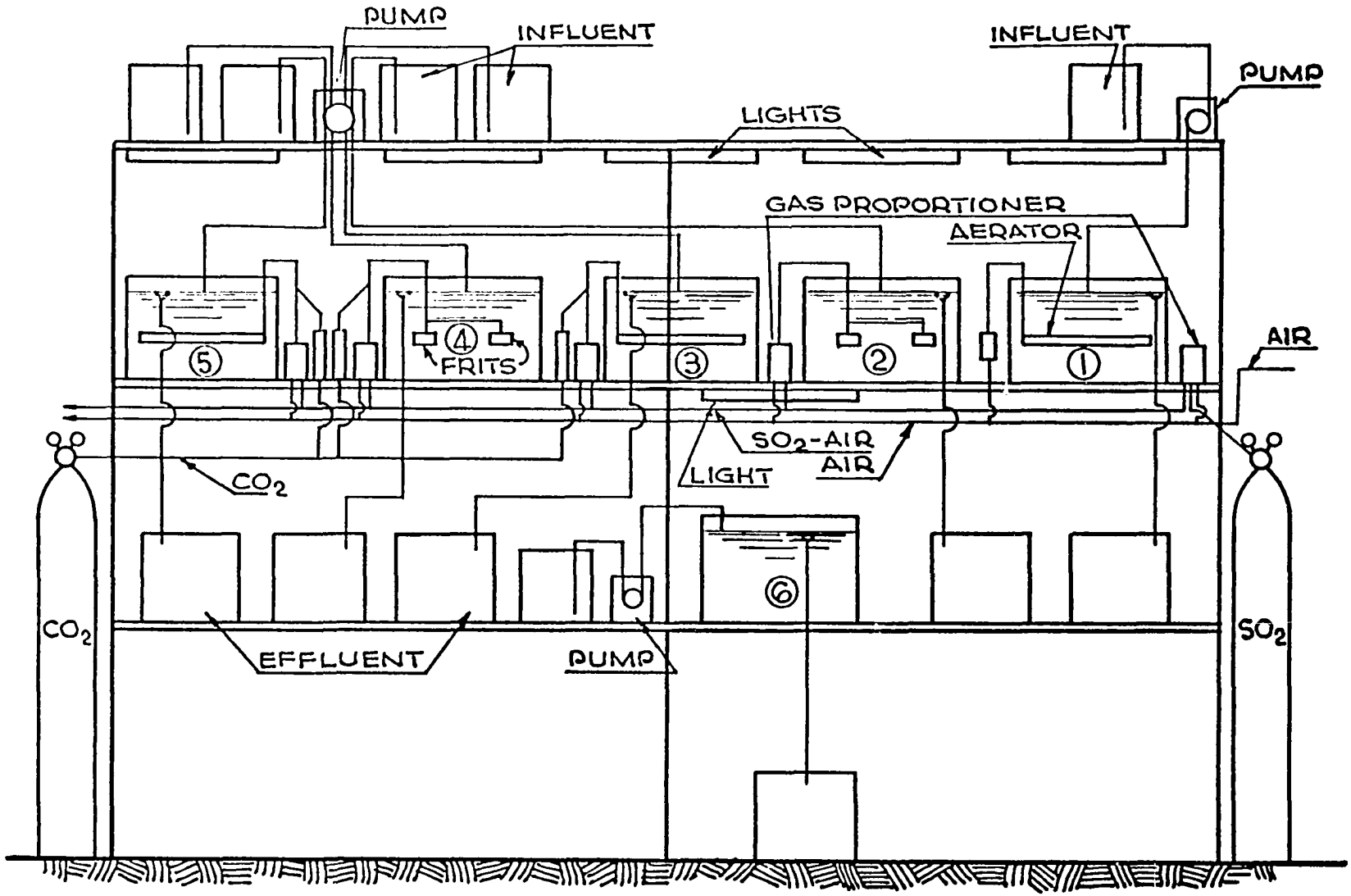

Figure 7--Arrangement of WSP and equipment in the laboratory.

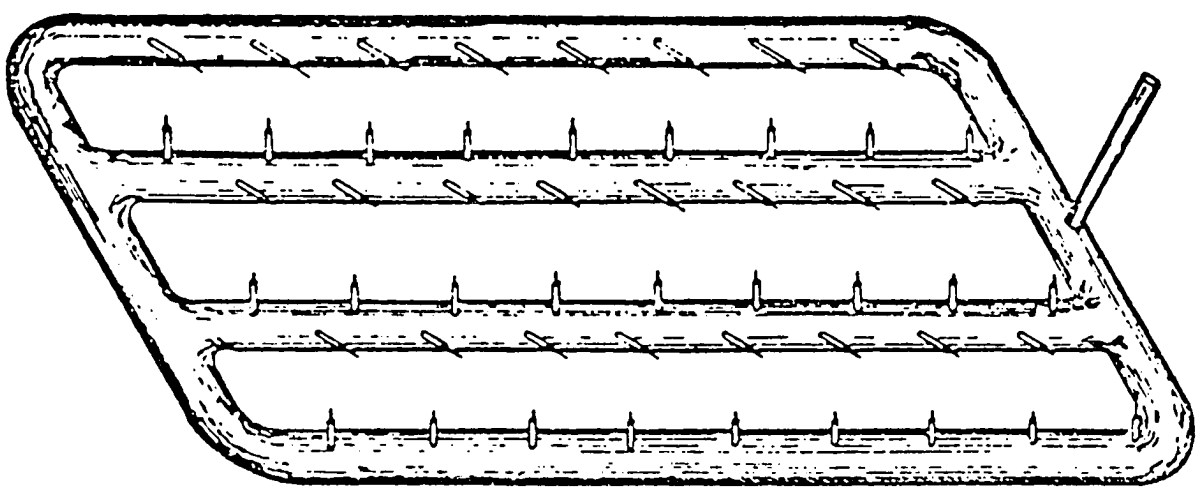

Figure 8--Aeration device for laboratory WSP (14).

every inch on the center lengths offset to give one needle for every inch.

Four of the six experimental ponds used in this study had been in various stages of operation and experimentation since 1968 (33). WSP-4 and WSP-5 received 500 ppm SO_2 at a rate of 0.3 lpm from December 1970 until July 1971 and WSP-3 received 1,000 ppm SO_2 at a rate of 1.3 lpm from March 1971 until July 1971. On 5 July 1971, WSP-2, WSP-3, WSP-4 and WSP-5 were placed in operation, each receiving 1,000 ppm SO_2 at a rate of 1 lpm. WSP-4 and WSP-5 also received 5 per cent CO_2 and WSP-3 received 10 per cent CO_2, which was metered into the air-SO_2 stream by rotameters controlled by needle valves from a cylinder of CO_2 equipped with a single stage regulator. In addition, WSP-5 was heated to approximately 40° C. As previously described, WSP-1 was aerated with air at 1 lpm and served as a control pond. A hydraulic feeding rate of 8 lpd was maintained continuously and calculated to approximate the desired BOD loading rate of 150 lb/a/d. The ponds were allowed to acclimate during the period 5 July 1971 until 13 September 1971 at which time data collection was started. WSP-6 was placed in operation in October 1971 as a nonaerated pond to receive neutralized effluent from WSP-3. The above conditions were maintained from August 1971 until January 1972.

A four-channel Buchler peristaltic pump and two Sigmamotor pumps were used to feed raw domestic waste obtained from the effluent of the grit chamber of the Oklahoma City North Side Sewage Treatment Plant. All ponds except WSP-6 received the same influent which was collected from the sewage treatment plant every 4 or 5 days and stored under refrigeration until used. The separate reservoirs for each pond were scrubbed

before filling to loosen precipitated and settled solids which were added to the appropriate pond. The 24-hour effluent volume was recorded for each pond.

A cylinder of SO_2 supplied by the Matheson Gas Company and fitted with a noncorrosive Air Products regulator was used to dispense the gas into the 0.25-in copper tubing system. Matheson Gas Company gas proportioners, which were recalibrated with a wet-test meter, were used to obtain the desired concentration of SO_2 by diluting the pure SO_2 with compressed air. The SO_2 was first diluted to 10,000 ppm in air by a primary proportioner and then further diluted with air at each WSP by secondary proportioners to obtain the 1,000 ppm concentrations. Needle valves on the gas proportioners were used to control the flow rate and a needle valve at the vent was used to produce the back pressure necessary for aeration.

Analysis for elemental sulfur was conducted once each week during the first weeks of the project by an adaptation to a method reported by Maurice (60) in which hexane was used as the solvent. Benzene solutions of sulfur were found to absorb strongly at 280 mu and was used instead of hexane. A 50-ml sample of the pond effluent was filtered through 0.45-u membrane filters using the standard Millipore filtration unit. The filters were dried at room temperature and extracted for 6 to 8 hours in a Soxhlet extractor with purified benzene. The volume of the extract was made to 100 ml with benzene and the absorbance at 280 mu was measured in a Beckman DK-2 spectrophotometer using 1-cm quartz cells. Elemental sulfur analysis in the sludge layer was not conducted, since previous studies indicated that none was present (33).

Sulfates were determined turbidimetrically on the influent and effluent of each WSP, on a daily basis early in the experiments and at least weekly throughout the course of the project, by means of the procedures outlined by the Hach Chemical Company (61) using the DR spectrometer.

Analysis for $SO_3^=$ was conducted almost every week, according to the potassium iodide-iodate titration method in Standard Methods for the Examination of Water and Wastewater (62).

Analytical methods in this reference were also used to analyze for $S^=$, BOD and total organic nitrogen. Analysis for $S^=$ was conducted once each day for the first week of the project and about once each week thereafter. Determinations of BOD and total organic nitrogen were made at least two times each week on all pond influents and effluents. All samples for BOD determinations which were lower than pH 6.0 were neutralized with a minimum volume of concentrated sodium hydroxide to pH 7.0 to 8.0 and seeded with diluted sewage to reduce interference during the organic stabilization process.

Dissolved SO_2 was determined once each week on WSP-2, WSP-3, and WSP-4 by use of the reagents in the West and Gaeke method as described in Selected Methods for the Measurement of Air Pollutants (63). The pond effluent was diluted 1.0 ml to 9.0 ml of distilled water and a 0.1 ml sample of the diluted pond effluent was added to 9.9 ml of sodium tetrachloromercurate followed by 1.0 ml of acid-bleached pararosaniline solution and 1.0 ml of 0.2 per cent formaldehyde solution. The samples were mixed and allowed to stand for 20 minutes for color development and then read at 560 mu using the blank as the reference.

A Beckman expanded scale pH meter was used to determine the pH of the ponds each day throughout the course of the project. Temperature readings were made daily with a laboratory thermometer centered over each pond with the bulb suspended about 2 in below the surface of the liquid.

CHAPTER V

RESULTS AND DISCUSSIONS

Frequent analyses of the air above the surface of the ponds revealed only trace amounts of SO_2 escaping from the liquid phase, thus indicating that the SO_2 was effectively removed from the air stream by the waste stabilization ponds. This observation was in close agreement with previous studies by Hobson et al. (14) on the removal of SO_2 from an air stream using the WSP and led to the questions concerning the mechanisms of removal, the molecular transformations of SO_2 occurring, and the role and fate of the sulfur compounds formed. These factors ultimately determine the practicality and applicability of the process for removing SO_2 with a liquid-carried waste treatment method.

The results of the $SO_4^=$, $SO_3^=$, $S^=$ and dissolved SO_2 analyses conducted during the course of this investigation are tabulated in the Appendix and are summarized in Table 2. A study of this table reveals that perceptible amounts of $SO_3^=$ and $S^=$ were absent in all ponds through which SO_2 was bubbled. This indicated that the compound sulfurous acid (H_2SO_3) was either not formed in measureable quantities from the reaction of SO_2 with water in the presence of dissolved oxygen (DO) or, due to a high DO and low pH, the $SO_3^=$ from the H_2SO_3 was rapidly oxidized to $SO_4^=$. The latter appears to be more plausible. This theory is supported by the enthalpy (ΔH) of formation of sulfuric acid from elemental sulfur in

TABLE 2

MEAN CONCENTRATION AND STANDARD DEVIATION OF SULFATE, SULFITE, SULFIDE, AND DISSOLVED SULFUR DIOXIDE IN WSP

ANALYSIS		Conc. in mg/l in Inf. and Eff. of Indicated WSP #						
		INF	1	2	3	4	5	6
$SO_4^=$	$\bar{x}$	257	237	1804	1859	1672	2385	1745
	s	39	54	276	241	237	254	307
	n	41	41	41	41	41	41	32
$SO_3^=$	$\bar{x}$	3.7						
	s	1.8	ND	ND	ND	ND	ND	ND
	n	12						
$S^=$	$\bar{x}$	4.9	1.6					2.1
	s	2.3	1.0	ND	ND	ND	ND	1.1
	n	27	27					23
DISSOLVED	$\bar{x}$			76	59	55	29	
SO_2	s	-	-	6.5	5.5	7.0	4.2	-
	n			16	16	16	16	

ND = Not detected at limit of method used: SO_3 (0.5 mg/l), $S^=$ (1.0 mg/l)

$\bar{x}$ = Mean

s = Standard deviation

n = Number of observations

which the transitions were shown to occur spontaneously in aqueous solutions in the presence of a catalyst. For the nonaerated WSP-6, which had an average pH of 7.4, algal growth, through the process of photosynthesis, aided in maintaining an aerobic zone, thus providing the oxygen necessary to convert any influent $SO_3^=$ to $SO_4^=$. WSP-1 was comparatively low in algae and had a relatively high pH of 7.36, but the aeration with air at the rate of 1 lpm established strong aerobic conditions and the excess DO in WSP-1 was available for oxidizing the influent $SO_3^=$ to $SO_4^=$.

Based on these observations, both pH and DO of the ponds may have been important factors in the reactions involved in the conversion of $SO_3^=$ to $SO_4^=$, but it appeared that DO was the controlling factor.

As previously illustrated in Figure 6, any soluble sulfides in those ponds that received SO_2 should have existed as hydrogen sulfide (H_2S) due to the relatively high H^+ concentration. The pH of the liquid in WSP-2, WSP-3, WSP-4 and WSP-5 was low as shown in the Appendix and summarized in Table 3; consequently, some H_2S in these ponds was expected. The fact that none was observed, even though small amounts were added through the liquid feed, supports the theory of the rapid oxidation of sulfur compounds to sulfate under aerobic, low pH conditions. Only WSP-1 and WSP-6, which were aerobic but had a relatively low H^+ concentration, exhibited any sulfide level and these were quite low, again emphasizing the effectiveness of the oxidation system in effect in the WSP. Such a system could have been established as follows:

$$2H_2S + 3\ O_2 \longrightarrow 2SO_3^= + 4H^+$$

$$2SO_3^= + O_2 \longrightarrow 2SO_4^=$$

in which case the $SO_3^=$ would be very rapidly oxidized to $SO_4^=$ as shown

TABLE 3

SUMMARY OF WSP OPERATING PARAMETERS

		INF	WSP-1	WSP-2	WSP-3	WSP-4	WSP-5	WSP-6
CONCENTRATION SO_2 (ppm)		-	-	1000	1000	1000	1000	-
CONCENTRATION CO_2 (per cent)		-	-	-	10	5	5	-
AERATION RATE (lpm)		-	1.0	1.0	1.0	1.0	1.0	-
pH	$\bar{x}$	7.07	7.36	1.92	1.88	1.92	1.73	7.24
	s	.23	.25	.13	.13	.12	.14	.19
	n	75	75	75	75	75	75	68
TEMPERATURE (°C.)	$\bar{x}$	-	22.6	22.6	22.9	22.9	40.2	22.6
	s	-	.9	1.1	1.1	1.2	1.2	.9
	n	-	75	75	75	75	75	68
EFFLUENT VOLUME (l)	$\bar{x}$	-	-	3.7	3.8	4.1	3.0	-
	s	-	-	.2	.1	.1	.1	-
	n	-	-	17	17	17	17	-

$\bar{x}$ = Mean

s = Standard deviation

n = Number of observations

in the second reaction. This again is indicative of the role of oxygen in sulfur reactions.

It was thought that elemental sulfur could have been formed at some stage in the process such as the reaction between the H_2S introduced through the feed and the DO present in the ponds; however, suspended elemental sulfur was not detected by use of the procedure previously described. Again, the presence of DO and the low pH in the ponds provided a favorable media for the oxidation of sulfur to $SO_4^=$. The following reaction illustrates a mechanism for elemental sulfur production under strict anaerobic conditions:

$$SO_4^= + 3H_2S + 2H^+ \longrightarrow 4S + 4H_2O$$

However, this reaction did not appear to take place in any portion of the ponds. The absence of H_2S and the presence of DO apparently prevented sulfur formation by this reaction. The above reaction also suggests that the aerobic zone of the ponds may have extended deeper into the liquid than expected and may have included part of the sludge layer.

The majority of the SO_2 entrained in the WSP was oxidized to $SO_4^=$ as shown in Table 2. This helped to verify the hypothesis that the $SO_4^=$ ion would be the predominant sulfur form when SO_2 was scrubbed into a complex matrix such as a WSP. The mechanisms for the oxidation of SO_2 to $SO_4^=$ in the WSP are not characterized simply. Superimposed on the many physical-chemical variables are effects due to microbiological activity. A simplified reaction for $SO_4^=$ formation is represented by the following:

$$3SO_2 + 3H_2O + 2\ O_2 + (m) \xrightarrow{Pt} 2H_2SO_4 + (m)SO_4 + H_2O$$

in which (m) represents ions such as calcium, magnesium, iron, manganese,

etc. and Pt represents catalytic activity. The catalyst could be organic compounds or metal ions such as cobalt, copper, vanadium and other materials which promote the oxidation process.

By comparing the mean $SO_4^=$ values, shown in Table 2, in WSP-5 to the mean values in the other WSP receiving SO_2, it could be seen that the $SO_4^=$ concentration (mg/l) was considerably higher. This was primarily due to the increased temperature in WSP-5 which caused a higher evaporation rate and lower liquid effluent volume. The elevated temperature could also have enhanced chemical and biochemical reactions and increased $SO_4^=$ solubilities.

The data for the analysis of the two principal inorganic sulfur species in the pond influents and effluents are summarized in Table 4 in the form of a sulfur balance. These balances were computed to elemental sulfur from observed $SO_4^=$ and dissolved SO_2 effluent concentrations and subtracted from the amount of sulfur entering the ponds from the air-SO_2 stream and from the liquid feed. The values indicate a slight enrichment of sulfur in the ponds. This small amount of unexplained sulfur could have deposited in the sludge layer, flowed out of the pond as one or several different sulfur species, or sulfur could have been incorporated as part of the biochemistry of microorganisms suspended in the liquid and embedded in the sludge.

The mean concentration of dissolved SO_2, as noted in Table 2, was less in the heated WSP-5 than in the other non-heated ponds that received SO_2. The solubility of gases in water tend to decrease with increased temperature. The CO_2 added to the air-SO_2 stream in WSP-3, WSP-4 and WSP-5 appeared to have little effect on the dissolved SO_2

TABLE 4

SULFUR BALANCE IN WSP

	WSP-2	WSP-3	WSP-4	WSP-5
EFFLUENT VOLUME (l)	3.7	3.8	4.1	3.0
EFFLUENT SO_4 (mg)	6674	7064	6855	7155
EFFLUENT SO_4 CALC. AS S (mg)	2225	2351	2285	2385
EFFLUENT DISSOLVED SO_2 (mg)	281	224	226	87
EFFLUENT SO_2 CALC. AS S (mg)	141	112	113	44
EFFLUENT TOTAL S (mg)	2366	2463	2398	2429
INFLUENT TOTAL S[a] (mg)	2566	2566	2566	2566
EFF/INF (100)[b] (mg S)	92.2	95.9	93.4	94.7

[a]1,000 ppm SO_2 equivalent to 2.612 mg SO_2/l (1881 mg S/d) at 25° C. and 760 mm Hg.

[b]Percentage influent sulfur appearing in the effluent.

concentration. It was thought that CO_2 would act only as a carrier gas and sweep dissolved SO_2 from the pond. Although the amount of dissolved SO_2 is small compared to the amount of $SO_4^=$, it would be an undesirable constituent of effluents entering a limited flow and low volume water course. It would compete for available oxygen in streams, impart H^+ ions to lower the pH of the receiving water and be toxic to certain biota.

The performance of the WSP, on a long term basis, was monitored by analyzing the influent and effluent liquid for BOD and organic nitrogen, by recording the pH and temperature of the liquid in the ponds, and by observing the appearance of the pond and occurrence of odors from the ponds. Reduction of BOD in the WSP was probably the best indicator of WSP function in terms of its ability to stabilize liquid-carried waste. Table 5 is a summary of the tabulated data from the Appendix showing the mean and standard deviation of the BOD values and the percentage BOD reduction.

The mean influent BOD was 265 mg/l with a standard deviation of 165 mg/l. The large standard deviation for the influent BOD indicated that the BOD at the sewage treatment plant fluctuated considerably and that this fluctuation was carried on to the ponds. Feeding the raw domestic waste with the highly variable BOD permitted the observation for the effects of shock load on the WSP. The ponds continued to reduce BOD throughout the course of the project and remain essentially odor free, thus indicating a high threshold toward shock loading.

The mean effluent BOD of the control pond (WSP-1) effluent, when compared to the mean influent BOD shown in Table 5, indicated slightly over 94 per cent BOD reduction which was considered excellent

TABLE 5

MEAN CONCENTRATION, STANDARD DEVIATION AND PERCENTAGE REDUCTION OF INFLUENT AND EFFLUENT BOD AND ORGANIC NITROGEN

WSP #		BOD (mg/l)			ORGANIC NITROGEN (mg/l)		
		INFLUENT	EFFLUENT	PERCENTAGE REDUCTION	INFLUENT	EFFLUENT	PERCENTAGE REDUCTION
1	$\bar{x}$	265	16	93.9	35.6	6.7	81.2
	s	165	13		11.6	3.5	
	n	41	41		27	27	
2	$\bar{x}$	265	58	78.1	35.6	30.9	13.2
	s	165	24		11.6	7.7	
	n	41	41		27	27	
3	$\bar{x}$	265	78	70.9	35.6	31.7	10.9
	s	165	35		11.6	7.3	
	n	41	41		27	27	
4	$\bar{x}$	265	81	69.4	35.6	32.3	8.8
	s	165	33		11.6	8.5	
	n	41	41		27	27	
5	$\bar{x}$	265	40	84.9	35.6	47.1	-32.3
	s	165	24		11.6	12.2	
	n	41	41		27	27	
6	$\bar{x}$	77	11	85.7	31.7	10.7	66.2
	s	34	10		7.3	5.4	
	n	41	39		27	23	

$\bar{x}$ = Mean s = Standard deviation n = Number of observations

for a single cell, aerated WSP. The slightly more than 81 per cent reduction of influent organic nitrogen also indicated that the control pond was functioning properly.

For WSP-2, which received 1,000 ppm SO_2 at 1 lpm, the mean effluent BOD value of 58 mg/l represents a treatment efficiency of about 78 per cent, and indicates that scrubbing SO_2 into the pond did have an effect on the waste stabilization process. However, a 78 per cent BOD reduction for a single-cell pond, operated under the conditions specified, was considered satisfactory. The marked difference between the organic nitrogen reduction values of WSP-1 and WSP-2 indicates that the low pH conditions in the SO_2-ponds caused a drastic change in the microbiological population and/or delayed nitrification in the stabilization process as discussed by Babbit and Baumann (64). Therefore, the BOD reduction in the ponds that received SO_2 was due almost entirely to stabilization of carbonaceous matter with little or no stabilization of the nitrogenous substances.

WSP-3 and WSP-4 received 1,000 ppm SO_2 with 10 and 5 per cent CO_2 added respectively to the air-SO_2 stream. A comparison of these two ponds with each other showed that the different concentration of CO_2 appeared to have no appreciable effect on BOD removal. However, a comparison of either WSP-3 or WSP-4 with the SO_2 control pond (WSP-2) indicated that CO_2 was involved in additional interference of BOD removal. This was thought to be partly due to a reduction of the amount of oxygen in the air-SO_2 stream which resulted in slightly less oxygen available for the oxidation of the organic waste.

WSP-5 was aerated with 1,000 ppm SO_2 and 5 per cent CO_2 at the

rate of 1 lpm, and the pond temperature was elevated as shown in the pond operating parameters in Table 3. A comparison of WSP-5 and WSP-4 indicates that, with both ponds receiving the same gases at the same rate, temperature had a beneficial effect on BOD removal (Table 5). The BOD reduction increased from near 69 per cent to about 85 per cent or an increase of nearly 24 per cent. This implies that the temperature of hot stack gases may be regulated in a manner beneficial to the treatment process. The increase in organic nitrogen in WSP-5 compared to WSP-4 indicated the possible presence of nitrogen-fixing organisms in WSP-5. The fungi are a group of organisms capable of functioning in an acid media and they could be the organisms involved in nitrogen fixation as well as enhancing BOD reduction.

The effluents of the ponds containing SO_2 were relatively high in H^+ concentrations and could not be considered suitable for discharge into the environment. WSP-6 was placed into operation as a nonaerated WSP designed to receive the neutralized effluent of one of the SO_2-ponds (WSP-3), thus expanding the overall environmental control method in order to produce a better quality effluent. The effluent from WSP-3 was neutralized to pH 7.0 to 7.5 by adding a minimum volume of a slurry of calcium hydroxide. The lime reacted with the dissolved SO_2 and $SO_4^=$ to precipitate calcium sulfate.

The percentage reduction of BOD and organic nitrogen in WSP-6, and the essentially neutral pH of the effluent, indicates the potential benefit of using a multi-cell pond arrangement in the environmental control system. This could be of future interest in the further development of this type of control method. For example, it may be advantageous to

use raw sewage as a stack scrubbing liquid followed by a neutralization and settling basin whose effluent feeds a polishing pond. It might be economically feasible to collect the sulfur-enriched precipitate from the neutralized effluent of the scrubbing ponds and subject the precipitate to anaerobic digestion to produce large quantities of hydrogen sulfide from which elemental sulfur could be easily recovered for marketing. It may also be possible to treat raw sewage in a WSP and use the effluent to scrub stack gases. The mixture of sewage and stack gases could then be neutralized with lime followed by an additional WSP for additional stabilization by microbes. The feasibility of incorporating any one or a combination of the above suggested arrangements into an acceptable control system must consider the economics involved. It appears that this concept of environmental pollution control may offer economic advantages over separate more costly systems now in use.

CHAPTER VI

SUMMARY AND CONCLUSIONS

This research was designed to investigate the mechanisms of transformation and nature and distribution of sulfur compounds formed after SO_2 was scrubbed from an air stream into waste stabilization ponds; to evaluate the performance of such WSP over an extended time period and observe the effect of adding CO_2 to the air-SO_2 stream. Four of the six WSP operated were dosed with 1,000 ppm SO_2 at 1 lpm, and three of the WSP that received SO_2 also received CO_2. One of the latter WSP was heated to approximately 40° C to simulate the effects of hot stack gases. One WSP was aerated with air only at 1 lpm and served as a control, while a sixth nonaerated pond functioned as a polishing pond that received neutralized effluent from a pond used to scrub SO_2.

In order to determine the fate of the SO_2 scrubbed into the ponds, analyses were conducted on the WSP influent and effluent, after a 2-month acclimation period, for $SO_4^=$, $SO_3^=$, $S^=$, elemental sulfur, and dissolved SO_2 over a 3-month period. The effects on WSP performance were evaluated by determining the BOD, organic nitrogen, pH and observing the appearance of the pond and the occurrence of any odor in the pond.

Based on the results of these analyses and observations the following conclusions have been drawn:

1. Sulfur dioxide at a concentration of 1,000 ppm was effectively

removed from an air stream by use of WSP, and the WSP continued to perform at a reasonable level of BOD reduction.

2. The principal forms of sulfur compounds found in the WSP effluents were sulfates and dissolved SO_2. No sulfites, sulfides, or elemental sulfur could be detected in the ponds receiving SO_2. In order to recover marketable sulfur additional treatment of the sulfate enriched effluent, such as anaerobic digestion to produce hydrogen sulfide from which elemental sulfur may be obtained, might be required. Since the SO_2 scrubbed into the ponds was transformed principally into soluble sulfates and wasted in the effluent in those forms, the ponds could be expected to continue functioning as an SO_2 scrubbing device and an effective treatment method to remove BOD.
3. Increasing the temperature of the pond contents to simulate aeration with hot stack gases improved the treatment efficiency in terms of BOD removal and reduced the amount of dissolved SO_2 in the effluent liquid.
4. The addition of CO_2 to the air-SO_2 stream appeared to interfere with BOD removal, but had only minimal effect on the amount of dissolved SO_2 in the ponds.
5. The performance of the WSP as measured by BOD and organic nitrogen reductions and effluent pH was considered acceptable only in terms of BOD reductions. Stabilization of nitrogenous matter essentially ceased in the equilibrated ponds under low pH conditions. Therefore the BOD reduction primarily reflected degradation of carbonaceous matter with little input from nitrification.

6. The WSP effluents that contained comparatively high hydrogen ion concentrations and relatively small amounts of dissolved SO_2, which was probably transient in the presence of dissolved oxygen, would be considered unsatisfactory for direct discharge into the environment. The dissolved SO_2, in addition to supplying additional hydrogen ions to the aqueous media, would be toxic to certain biota.
7. The effluent from the WSP that received SO_2, and considered unsuitable for direct discharge, could be neutralized with lime and subjected to additional stabilization to yield an effluent acceptable for discharge to the environment. One possible adaptation of the combined environmental control concept would be to operate multi-cell ponds. Stack gases may be bubbled into a scrubbing pond and the effluent liquid neutralized and treated in an additional WSP. Further studies should be conducted on a number of combinations and WSP arrangements. It may be advantageous to use raw sewage to scrub gases from a stack followed by neutralization of the liquid and subsequent stabilization in WSP.

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APPENDIX

TABLE 6

INFLUENT SULFITE ANALYSES

SAMPLE #	Conc. of $SO_3^=$ (mg/l)[a]
2191	4.6
1101	2.2
8101	3.4
12101	2.8
26101	5.7
2111	8.3
9111	2.5
17111	3.6
30111	4.3
8121	2.4
10121	2.0
0612	2.3
$\bar{x}$	3.7
s	1.8
n	12

[a]Sulfites were not detected in WSP-1, WSP-2, WSP-3, WSP-4, WSP-5 nor WSP-6 at the limit of detection of the method used (1.0 mg/l).

TABLE 7

INFLUENT AND EFFLUENT SULFIDE ANALYSES

SAMPLE #	Conc. in mg/l[a]		
	INF SULFIDE	WSP-1	WSP-6
1391	4.2	1.2	-
1491	2.4	2.5	-
1591	8.0	4.4	-
1691	4.8	.8	-
2091	8.0	.5	3.2
2291	3.2	1.2	3.0
2491	6.4	3.2	4.0
2791	4.0	.5	2.4
3091	3.2	.5	1.6
4101	5.6	2.5	3.2
7101	6.8	.8	4.2
12121	2.4	.7	1.2
15101	2.1	.5	2.4
20101	4.2	1.5	3.6
21101	9.6	1.0	1.5
26101	2.4	.5	1.2
1111	3.6	ND[b]	1.0
3111	6.4	.5	1.2
8111	5.6	ND	2.4
16111	2.4	.5	3.2
19111	9.8	1.2	2.1
26111	7.2	ND	.5
30111	2.8	.5	1.6
1121	3.2	.5	1.2
7121	4.0	1.2	.5
14121	3.2	.5	1.6
0512	7.2	ND	1.2
$\bar{x}$	4.9	1.0	2.1
s	2.3	.9	1.1
n	27	27	23

[a]Sulfide was not detected in WSP-2, WSP-3, WSP-4 and WSP-5 at limit of detection of the method used (.5 mg/l).

[b]0.25 mg/l, the mid-point between 0.0 mg/l and the detection limit of 0.5 mg/l was used to compute $\bar{x}$ and s.

TABLE 8

EFFLUENT DISSOLVED SULFUR DIOXIDE ANALYSES

SAMPLE #	Conc. in mg/l for Indicated WSP #[a]			
	2	3	4	5
1391	87	62	66	34
2191	69	58	53	28
2391	73	64	62	36
1101	82	72	56	31
5101	72	65	47	24
12101	68	56	54	28
19101	84	61	61	32
25101	70	54	54	23
2111	77	58	45	36
9111	83	62	56	28
16111	69	55	54	22
19111	72	48	58	29
30111	84	52	46	31
10121	76	58	44	26
16121	68	60	57	30
0412	83	64	69	34
$\bar{x}$	76	59	55	29
s	7	6	7	4
n	16	16	16	16

[a]Pond that received 1,000 ppm SO_2 at 1 lpm.

TABLE 9

INFLUENT AND EFFLUENT SULFATE ANALYSES

SAMPLE #	Conc. in mg/l for Indicated WSP #						
	INF	1	2	3	4	5	6
1391	250	285	1850	2050	1200	2400	-
1491	250	150	1600	2000	1750	2400	-
1591	225	250	1250	1800	1750	2500	-
1691	250	250	1650	1700	1800	2200	-
1791	275	350	1650	1950	1750	2400	-
2091	200	250	1700	1850	1950	2450	-
2191	285	200	1750	1850	1800	1900	-
2291	300	250	2000	2200	2000	2500	-
2391	300	285	1650	1850	1700	2300	-
2491	300	260	2000	2500	1450	2000	1300
2791	350	250	1850	2100	1400	2400	1200
2891	250	300	1950	2050	1850	2250	1300
2991	225	225	1750	1900	1800	2450	1500
3091	300	250	1650	1950	1300	2600	1700
4101	250	200	2050	2100	1500	2200	1500
5101	200	250	1950	1850	1700	2450	1500
6101	250	200	1800	1900	1850	2350	1550
7101	250	150	1500	1850	1600	2300	1700
11101	225	250	2000	1800	1750	3250	1800
13101	200	225	1700	1850	1750	2650	1750
19101	250	200	1650	1750	1550	2300	1800
20101	250	250	1950	1700	1450	2400	1850
21101	225	200	1750	1850	1700	2400	1800
28101	300	350	2450	2600	1000	2950	1650
1111	350	250	2050	2000	1750	2250	1900
4111	350	350	1650	1650	1600	2450	1750
8111	250	200	2050	1750	1600	2200	1800
11111	250	250	1950	1700	1850	2400	2150
15111	250	150	2000	1850	2050	2400	2050
18111	200	200	2350	1450	2100	2550	2450
22111	225	150	2450	2000	1950	2650	2300
29111	250	200	2350	2100	2600	2150	-
2121	300	150	1650	1750	1400	1800	2150
6121	300	200	1350	1250	1800	2650	1500
9121	225	350	1400	1650	1600	2500	1750

TABLE 9--Continued

SAMPLE #	Conc. in mg/l for Indicated WSP #						
	INF	1	2	3	4	5	6
13121	225	200	1650	1750	1450	2050	1950
0312	250	300	1450	1500	1300	2300	1900
0612	250	250	1650	1700	1600	2500	1450
0712	250	250	1600	1700	1700	2300	1100
0812	250	200	1700	1650	1800	2100	1700
0912	200	250	1600	1800	1550	2100	1900
$\bar{x}$	257	237	1804	1859	1672	2385	1745
s	39	54	276	241	237	254	307
n	41	41	41	41	41	41	32

TABLE 10

INFLUENT AND EFFLUENT BOD ANALYSES

SAMPLE #	Conc. in mg/l for Indicated WSP #						
	INF	1	2	3	4	5	6
1391	315	5	18	31	45	9	-
1591	221	14	36	41	45	21	-
2091	74	14	78	90	95	42	28
2491	391	12	32	50	33	19	14
2791	221	7	48	50	27	31	13
3091	78	12	48	82	97	41	21
4101	257	16	74	1	90	13	10
6101	129	1	41	61	126	30	2
7101	429	28	62	150	175	118	36
8101	235	17	66	117	100	70	30
13101	149	12	63	123	90	51	21
14101	128	8	81	177	107	73	22
15101	247	1	55	93	76	25	10
18101	286	3	91	78	76	43	1
20101	81	1	75	71	53	49	2
21101	684	8	91	90	96	54	23
22101	190	10	91	90	81	41	9
27101	379	4	47	71	65	38	22
28101	450	18	52	61	81	41	2
29101	178	16	29	94	77	64	17
3111	155	39	40	76	66	35	5
4111	104	39	19	83	85	61	7
5111	72	38	29	49	77	18	2
10111	540	56	35	91	123	16	8
11111	89	4	29	93	146	54	2
12111	120	35	41	82	101	15	2
17111	121	34	42	57	82	2	2
18111	303	21	92	71	83	43	15
19111	621	45	82	178	160	105	17
23111	521	13	64	36	56	20	22
25111	396	12	12	47	47	46	5
26111	568	19	61	69	33	28	19
1121	249	13	61	65	97	65	3
2121	226	7	101	91	88	57	7
3121	191	21	79	70	71	33	2

TABLE 10--Continued

SAMPLE #	INF	Conc. in mg/l for Indicated WSP #					
		1	2	3	4	5	6
15121	188	7	33	19	16	32	4
0512	576	14	61	88	54	14	6
0612	143	10	62	77	55	26	2
0712	270	13	82	82	68	24	5
0812	182	6	76	72	68	34	4
0912	110	3	97	80	107	49	3
$\bar{x}$	265	16	58	78	81	40	11
s	166	13	24	35	33	24	10
n	41	41	41	41	41	41	39

TABLE 11

INFLUENT AND EFFLUENT ORGANIC NITROGEN ANALYSES

SAMPLE #	Conc. in mg/l for Indicated WSP #						
	INF	1	2	3	4	5	
1391	32.0	5.6	19.6	15.7	11.2	59.	
1491	38.5	4.1	16.4	22.4	35.3		
1691	41.4	2.8	25.6	31.7	27.9		-
2291	46.5	6.1	29.0	25.2	31.9	[illegible]	-
2491	38.4	6.8	24.1	29.1	31.3	46.5	11.4
2791	35.0	5.6	17.4	31.4	20.0	49.3	20.0
3091	18.4	12.1	30.8	31.9	38.1	51.5	5.6
4101	43.1	6.5	36.0	31.0	40.3	42.0	8.6
7101	63.0	8.4	28.7	20.7	40.9	47.0	9.5
14101	19.5	4.3	39.2	26.3	18.7	40.6	5.6
20101	14.7	9.6	29.7	36.4	37.5	39.7	7.9
28101	53.6	5.6	31.3	24.8	26.5	43.7	8.5
1111	28.1	11.2	36.2	32.4	28.6	38.4	11.2
4111	21.5	8.4	37.5	36.4	37.8	62.7	19.6
8111	23.5	14.5	27.5	33.4	27.0	45.0	5.6
11111	16.3	2.8	26.5	23.2	21.3	24.5	2.0
15111	46.5	13.6	33.7	43.1	40.5	59.7	16.8
18111	49.8	5.6	47.6	45.3	51.6	78.8	11.7
22111	33.6	2.3	33.6	44.8	33.0	56.5	5.6
29111	35.0	5.6	28.5	40.9	33.6	58.8	20.1
2121	31.8	6.3	33.6	29.7	31.5	42.1	11.2
3121	34.1	8.9	48.3	34.1	32.4	57.1	17.4
6121	39.2	5.6	26.9	38.6	32.1	51.3	11.2
9121	49.7	2.8	35.6	30.3	27.2	46.5	17.4
13121	40.4	11.2	20.7	25.2	33.0	50.5	5.6
0612	33.0	5.6	32.5	40.3	56.9	53.8	10.1
0812	35.7	2.8	38.1	31.9	48.1	21.8	2.9
$\bar{x}$	35.6	6.7	30.9	31.7	32.3	47.1	10.7
s	11.6	3.5	7.7	7.3	8.5	12.1	5.4
n	27	27	27	27	27	27	23

TABLE 12

WSP EFFLUENT VOLUME

SAMPLE #	Volume (l) of Effluent from Indicated WSP #			
	2	3	4	5
1391	4.0	3.9	4.0	3.1
1491	3.9	3.7	3.9	3.0
1591	4.0	3.7	4.0	3.1
1691	3.9	3.8	4.1	3.0
2391	3.8	3.9	4.2	2.9
2891	3.7	3.8	4.1	2.9
1101	3.6	3.9	4.2	2.9
5101	3.6	4.0	4.3	3.0
6101	3.6	3.9	4.1	3.1
11101	3.5	3.7	4.1	3.0
14101	3.5	3.8	4.2	3.1
18101	3.6	3.7	4.1	3.0
25101	3.6	3.8	4.0	2.9
3111	3.7	3.9	4.0	3.0
5111	3.6	3.8	4.1	3.1
10111	3.8	3.9	4.2	3.1
12111	3.7	3.8	4.1	3.0
$\bar{x}$	3.7	3.8	4.1	3.0
s	.2	.1	.1	.1
n	17	17	17	17

TABLE 13

INFLUENT AND EFFLUENT pH

SAMPLE #	pH of Inf. and Indicated WSP #						
	INF	1	2	3	4	5	6
1391	6.85	7.80	2.15	2.10	2.05	2.00	-
1491	6.90	7.60	2.25	2.10	2.05	1.95	-
1591	6.95	7.85	2.05	2.00	2.00	2.00	-
1691	6.85	7.75	2.15	2.00	1.95	1.90	-
1791	6.80	7.55	2.10	2.00	2.00	1.95	-
2091	7.25	7.40	2.20	2.10	2.20	2.00	-
2191	7.10	7.35	2.05	1.95	2.00	1.95	-
2291	7.25	7.65	1.90	1.75	1.90	1.80	6.90
2391	6.95	7.50	1.95	1.90	2.00	1.85	7.45
2491	7.10	7.70	1.95	1.80	1.95	1.80	7.60
2791	6.90	7.15	2.10	2.00	2.05	1.90	7.50
2891	6.85	7.40	2.05	1.95	2.00	1.90	7.25
2991	7.35	7.40	2.00	1.90	1.95	1.85	7.15
3091	7.30	6.95	2.15	2.05	2.10	1.95	7.05
1101	6.75	7.00	2.00	1.95	2.05	1.75	7.10
4101	6.95	6.90	2.20	1.85	2.05	1.75	7.20
5101	6.85	7.45	1.95	1.90	1.95	1.70	7.15
6101	7.05	7.35	1.90	1.90	1.95	1.75	6.95
7101	6.95	6.75	2.15	1.95	2.05	1.70	7.00
8101	6.95	6.95	2.05	2.00	1.95	1.65	7.05
11101	6.85	6.85	1.90	1.95	2.05	1.50	7.00
12101	7.05	7.10	1.85	1.80	1.90	1.65	7.30
13101	6.95	7.00	1.75	1.70	1.75	1.60	7.20
14101	7.20	7.05	1.75	1.80	1.85	1.70	7.30
15101	6.95	7.35	1.65	1.60	1.65	1.55	7.25
18101	6.95	7.10	1.70	1.65	1.70	1.60	7.25
19101	7.30	7.30	1.75	1.80	1.85	1.65	7.45
20101	7.10	7.35	1.80	1.85	1.90	1.75	7.20
21101	7.40	7.30	1.90	1.85	1.95	1.65	7.05
22101	7.05	7.10	1.75	1.60	1.70	1.50	7.35
25101	6.85	7.10	1.80	1.80	1.90	1.60	7.50
26101	7.15	7.10	1.85	1.70	1.80	1.65	7.10
27101	6.85	7.55	1.90	1.85	1.95	1.75	7.30
28101	6.90	7.50	1.85	1.80	2.00	1.70	7.20
29101	7.05	7.50	1.70	1.65	1.75	1.55	7.10
1111	7.05	7.60	1.80	1.65	1.75	1.55	7.10
2111	7.00	7.10	1.75	1.70	1.80	1.65	7.10
3111	6.95	7.05	1.80	1.85	1.95	1.70	7.05
4111	6.80	7.70	1.85	1.90	2.00	1.90	6.85
5111	7.35	7.50	1.85	1.90	2.00	1.85	7.25

TABLE 13--Continued

SAMPLE #	pH of Inf. and Indicated WSP #						
	INF	1	2	3	4	5	6
8111	6.30	7.70	1.80	1.85	1.85	1.65	7.60
9111	7.10	7.50	1.85	1.90	1.90	1.55	7.45
10111	7.85	7.40	1.75	1.70	1.80	1.50	7.05
11111	6.80	7.40	1.80	2.15	2.00	1.60	7.70
12111	7.30	7.05	1.85	1.95	1.80	1.60	7.35
15111	7.10	7.40	1.70	2.05	1.75	1.55	6.95
16111	7.35	7.40	1.90	1.75	1.80	1.50	7.05
17111	7.35	7.20	1.80	1.70	1.80	1.65	7.10
18111	7.25	7.60	1.80	2.00	1.70	1.60	6.95
19111	7.05	7.55	1.85	2.00	1.95	1.65	7.00
22111	7.10	7.35	1.95	1.75	1.90	1.55	7.05
23111	7.30	7.45	1.95	1.85	1.90	1.60	7.35
25111	7.60	7.35	1.80	1.85	1.70	1.55	7.35
26111	7.05	7.45	1.85	1.70	1.90	1.55	7.35
29111	7.10	7.30	1.85	1.80	1.65	1.50	7.10
30111	7.10	7.50	1.80	1.85	1.90	1.55	7.35
1121	6.85	7.35	2.05	2.00	1.95	1.80	7.45
2121	7.45	7.45	2.00	1.90	1.95	1.85	7.35
3121	6.90	7.85	2.05	1.90	2.05	1.75	7.00
6121	6.95	7.60	2.05	2.10	1.95	1.65	7.15
7121	6.95	7.35	1.95	2.00	2.05	1.75	7.30
8121	7.25	7.20	1.90	1.85	1.95	1.60	7.50
9121	6.80	7.45	2.00	1.90	2.05	1.95	7.40
10121	7.25	7.60	1.95	1.90	2.00	1.85	7.60
13121	7.65	7.60	2.05	2.00	2.10	1.85	7.05
14121	6.95	7.05	1.95	1.90	2.00	1.90	7.25
15121	7.20	7.05	1.95	1.85	1.95	1.80	7.35
16121	6.90	7.20	2.00	1.90	2.05	1.90	7.35
0312	7.25	7.50	1.95	2.05	1.85	1.90	7.40
0412	6.95	7.40	2.05	2.00	2.15	1.80	7.35
0512	7.20	7.20	1.95	1.75	1.85	1.75	7.35
0612	6.80	7.00	2.00	2.00	2.00	1.85	7.40
0712	7.00	7.65	1.90	1.85	1.95	1.85	7.25
0812	7.30	7.30	2.05	1.95	2.00	1.75	7.65
0912	7.25	7.45	2.00	2.00	2.00	1.65	7.25
$\bar{x}$	7.07	7.36	1.92	1.88	1.92	1.73	7.24
s	.23	.25	.13	.13	.12	.14	.19
n	75	75	75	75	75	75	68

TABLE 14

TEMPERATURE OF WSP CONTENTS

SAMPLE #	Temp. °C. of Indicated WSP #					
	1	2	3	4	5	6
1391	21	22	21	21	37	-
1491	22	22	21	22	40	-
1591	21	21	23	21	38	-
1691	21	21	22	21	39	-
1791	21	21	22	22	41	-
2091	22	21	22	22	39	-
2191	23	23	22	23	40	-
2291	22	21	22	22	39	22
2391	22	23	23	22	40	23
2491	23	24	23	25	42	23
2791	24	25	25	25	40	24
2891	23	24	23	24	39	23
2991	22	23	22	22	39	22
3091	22	21	22	22	38	22
1101	21	22	21	21	39	21
4101	22	21	22	22	39	22
5101	21	22	22	21	38	22
6101	22	23	22	23	40	23
7101	21	21	22	21	39	21
8101	23	23	22	22	40	21
11101	23	23	24	23	42	23
12101	22	22	23	23	41	23
13101	23	22	23	22	40	21
14101	22	21	22	22	39	21
15101	23	24	23	23	39	23
18101	22	22	21	22	40	21
19101	22	23	22	23	40	23
20101	22	21	22	22	39	21
21101	22	23	24	23	42	23
22101	23	23	24	24	41	22
25101	23	24	25	25	43	25
26101	23	22	23	23	40	23
27101	23	22	22	23	41	22
28101	24	24	25	24	42	23
29101	23	24	23	23	41	23
1111	24	24	25	25	40	23
2111	23	22	23	22	40	23
3111	22	23	22	22	42	23
4111	23	23	24	25	40	22
5111	23	22	22	23	39	22

TABLE 14--Continued

SAMPLE #	Temp. °C. of Indicated WSP #					
	1	2	3	4	5	6
8111	24	23	25	25	41	23
9111	23	24	23	23	41	23
10111	23	24	23	24	40	24
11111	24	24	25	24	41	24
12111	24	23	23	24	40	23
15111	22	23	22	22	42	22
16111	22	23	22	22	40	23
17111	22	22	23	22	40	23
18111	24	23	25	25	39	23
19111	23	23	24	24	41	23
22111	24	25	25	24	39	24
23111	23	22	22	22	40	23
25111	23	24	24	23	41	23
26111	22	23	22	23	41	23
29111	24	25	25	26	41	24
30111	23	22	23	23	39	23
1121	23	22	23	23	40	23
2121	22	23	23	22	40	23
3121	24	24	25	25	41	24
6121	23	22	22	23	40	22
7121	23	22	22	23	41	23
8121	23	22	23	23	41	23
9121	23	22	23	22	42	22
10121	24	24	23	22	41	22
13121	23	22	23	23	41	23
14121	23	24	23	23	41	23
15121	22	23	23	22	40	21
16121	25	24	26	25	41	24
0312	22	23	22	22	42	22
0412	23	22	23	22	41	22
0512	22	21	22	22	39	22
0612	22	23	23	23	40	22
0712	22	21	22	22	38	22
0812	23	22	23	23	40	22
0912	22	23	23	23	41	22
$\bar{x}$	22.6	22.6	22.9	22.9	40.2	22.6
s	.9	1.1	1.1	1.2	1.2	.9
n	75	75	75	75	75	68