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THE EFFECTIVENESS OF AERATION AND POTASSIUM PERMANGANATE OXIDATION AND FILTRATION ON REMOVAL OF IRON AND MANGANESE FROM GROUND WATER

BY

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1980

THE EFFECTIVENESS OF AERATION AND POTASSIUM PERMANGANATE OXIDATION AND FILTRATION ON REMOVAL OF IRON AND MANGANESE FROM GROUND WATER

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Dr. Dwayne A. Rollag
Head, Civil Engineering
Department, Thesis Adviser

Date

DEDICATION

This thesis is dedicated to the memory of my sister, Mary Helen Quail. Mary passed away May 3, 1979 at the age of 19, following a one year battle against cancer. The memories of our childhood together and Mary's radiant personality have sustained me through the writing of this thesis.

S. J. Quail

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INTRODUCTION

Nature of the Problem

The United States Public Health Service (USPHS) established water quality standards in 1946 and revised them in 1956 and 1962. In these standards the maximum recommended concentrations of iron and manganese were 0.3 and 0.05 mg/l respectively (1). Because trace amounts of these elements are essential for proper nutrition of both plants and animals, the recommended limits are not based on any physiological or environmental considerations (2)(3). Rather, the presence of iron and manganese in water is objectionable because the precipitation of these metals alters the appearance of the water, turning it a turbid yellow-brown to black. (4).

Additional problems associated with high concentrations of iron and manganese may include one or more of the following:

1. The water may have taste and/or odor due to the presence of these metals (2)(4).
2. Industrial products, such as paper and textiles, may become discolored due to the precipitates of these metals in the process water (5).
3. Household utensils, porcelain plumbing fixtures and clothes may become stained (4).
4. Industrial demineralizers for high-pressure boilers and home zeolite water softeners may become clogged reducing their efficiencies (4).
5. Deposition of precipitates in the distribution system will form a film on the pipe walls. This film can act as a catalyst and speed up the deposition of these metals. Increased deposition can reduce the pipe diameter and eventually clog the pipe. Also, when these precipitates are already in the mains and the flow throughout the distribution system is

increased, some of the precipitates can be resuspended, causing high turbidities (6).

6. Iron bacteria (e.g., Crenothrix and Leptothrix) and manganese bacteria (e.g., Pedomicrobium and Hyphomicrobium) can grow within the filters and distribution pipes, where they can seriously interfere with the service. Upon the death and decay of these organisms, bad odors and unpleasant tastes may be produced (4)(6)(7).

Scope and Objectives

The Brookings, South Dakota East Water Treatment Plant is primarily an iron and manganese removal plant. Present operation of the facility includes aeration, lime softening, alum coagulation, recarbonation, potassium permanganate oxidation, filtration, chlorination and fluoridation[1]. Iron and manganese in the plant effluent are within the USPHS recommended standards[2].

The purpose of this investigation was to determine if comparable iron and manganese removal can be achieved using only aeration, potassium permanganate oxidation and filtration. In this investigation, removal efficiencies and water stability were used as parameters of comparison.

A pilot unit was used in these investigations to avoid disruption of the East Plant operations. This pilot unit included the same units and filter media as the East Plant and was operated at the same detention times and filter rates. Both the East Plant and pilot unit received raw water from Well 1.

[1] Based on plant inspection.

[2] Based on inspection of plant operating records.

REVIEW OF LITERATURE

Chemistry of Iron and Manganese

Iron and manganese are adjacent to each other on the periodic table and because of this would be expected to be similar chemically. Manganese chemistry, however, is much more complex (8). Iron occurs in two oxidation states, as divalent ferrous iron or as trivalent ferric form (3), whereas, manganese can exist at any oxidation state from 0 to +7 (8). However, Bell stated that in most water supplies, only the +2, +3, +4, and +6 oxidation levels are likely to be encountered (9). Fine (8) explained this further, stating that Mn +6 is stable only in a strongly alkaline solution and when in a non-alkaline solution, tends to oxidize to Mn +7. In turn, Mn +7 tends to reduce to either the Mn +2 or Mn +4 depending upon the oxidation demand of the water.

Iron and manganese are generally in the ferrous (Fe +2) and manganous (Mn +2) states when found in natural waters. However, at low pH or high alkalinity, other forms can also occur in solution (10)(11). For example, ferric iron (Fe +3) can exist in concentrations greater than 0.01 mg/l at pH values below 5.0 (11).

Iron and manganese are the most abundant of the heavy metals and comprise roughly 5.0 and 0.1 percent of the lithosphere, respectively (3). Since manganese-bearing minerals are less abundant than iron-bearing minerals, manganese is usually found less frequently in natural waters than is iron. The concentrations of iron and manganese found in solution are frequently limited by the solubility of their carbonates. Because carbonates are less soluble at high alkalinity, waters with high alkalinity often have lower iron and manganese contents than waters of low alkalinity (4).

Iron and manganese, as well as other cations and anions in solution, are derived from solid-phase rock minerals with which the water has been in contact (12). Iron occurs in silicate minerals of igneous rocks such as pyroxenes, amphiboles, and some micas. Manganese, on the other hand, is found in greatest abundance in metamorphic and sedimentary rocks. Only small amounts of manganese can be found in igneous rocks. A list of iron and manganese-bearing minerals is presented in Table 1 (4). Oxides of iron and manganese will accumulate in soils as the more soluble constituents are leached from weathered rocks (4).

When water percolates through soil containing organic matter and aerobic organisms, the water is readily deprived of oxygen. These organisms produce carbon dioxide (CO_2) as a by-product, thereby introducing CO_2 into the water (4). Carbon dioxide in the water lowers the pH by converting the hydroxides to carbonates and the carbonates to bicarbonates and carbonic acid (13). Iron and manganese are also leached out of decaying plants and animals. This is especially true for plants, since manganese is an essential element in photosynthesis. Concentrations of 13 to 128 milligrams (mg) of manganese per kilogram (kg) of plant material have been extracted from leaves (14). Even though it is possible for iron and manganese to exist in solution in surface waters, it is not a common situation.

Table 1. Iron and Manganese-Bearing Minerals (4)

Formula	Mineralogical Name
$Fe_{0.95}O$	Wüsite
Fe_2O_3	Hematite
$2Fe_2O_3 \cdot 3H_2O$	Limonite
Fe_3O_4	Magnetite
FeS	Trolite
$FeCO_3$	Siderite
Fe_2SiO_4	Faylite
FeOOH	Goethite
MnO	Manganosite
Mn_3O_4	Hausmannite
γ-MnOOH	Manganite
β-MnO_2	Pyrolusite
$MnCO_3$	Phodochrosite
MnS	Albandite
$MnSiO_3$	Rodonite
Mn_2SiO_4	Tephroite

When dissolved oxygen comes in contact with dissolved iron and manganese the oxidation process begins:

$$\text{Fe}\ (+2) \rightarrow \text{Fe}\ (+3)\downarrow + e^- , \qquad (1)$$

$$\text{and Mn}\ (+2) + 2H_2O \rightarrow MnO_2\downarrow + 4H^+ + 2e^- . \qquad (2)$$

Iron and manganese are slowly oxidized to form insoluble precipitates. However, acid and anaerobic conditions create a reducing environment in which iron and manganese are converted from the insoluble to the soluble forms. An example of this is in acid mine wastes; where iron is reduced to the soluble state as a result of the acid conditions.

The relationship between the oxidized and reduced forms of iron and manganese is expressed by the Nernst Equation:

$$Eh = E^o + \frac{RT}{nF} \ln \frac{A_{ox}}{A_{red}} \qquad (3)$$

where:

Eh = Redox potential, millivolts (mv)

E^o = Standard oxidation potential, mv

i.e. for $Fe\ (+2) \rightarrow Fe\ (+3) + e^-$; $E^o = +0.881$ mv
$Mn\ (+2) + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$; $E = +1.230$mv

R = Universal gas Constant; 1.987 cal/degree Mole

T = Temperature; degrees Kelvin

n = Number of electrons involved in the reaction

F = Faraday constant, 96,484 absolute coulombs

A_{ox} = Activity of oxidized forms of ions

A_{red} = Activity of reduced forms of ions

Exact analysis of the redox potential requires the actual activity of the ions, however, the ionic concentrations are generally so small that they can be used as approximations of the activity. Thus by inserting the appropriate constants and using ionic concentrations instead of activities, the Nernst equation for iron may be written (15)(16):

$$Eh = 0.771 + 0.0592 \log \frac{Fe\ (+3)}{Fe\ (+2)}; \qquad (4)$$

and for manganese (+2 state to +4 state)

$$Eh = 1,230 + \frac{0.0592}{2} \log \frac{Mn\,(+4)}{Mn\,(+2)} \qquad (5)$$

An understanding of redox equations can be helpful in determining whether a particular reaction is possible under given environmental conditions and in evaluating how conditions might be altered to encourage desirable transformations (i.e. Fe +2 → Fe +3) or prevent undesirable reactions (i.e. Mn +4 → Mn +2). Theoretically, the possibility for further oxidation can be determined. With this information, methods could be optimized to produce the best removals assuming equilibrium conditions. However, conversion of iron and manganese to the insoluble form is also dependent on the reaction rates. Factors which influence the rate of oxidation are summarized in Table 2.

Table 2. Factors Affecting the Rate of Iron and Manganese Oxidation. (5)

PHYSICAL

1. An increase in temperature will speed up the oxidation reaction and a decrease in temperature will slow the reaction.

2. Detention time following the oxidation process will determine how complete the redox reactions occur.

CHEMICAL

1. A low pH following the addition of an oxidant may slow the reaction (for iron, pH less than 6 and for manganese, pH less than 9.5). (3)

2. Highly alkaline waters often have lower iron and manganese concentrations than waters with low alkalinity.

3. The solubility of iron and manganese is altered by the presence of anionic constituents such as chlorides, nitrates, phosphates.
4. The catalytic effect of other cations in the water, such as copper and aluminum, tend to accelerate the oxidation reactions of iron and manganese.
5. The more dissolved oxygen present in the water, the faster the oxidation reactions proceed.
6. The presence of complex-forming organic material combines with the iron and manganese thus slowing the oxidation process.

All of these factors affect removal methods differently and the net result cannot be anticipated from chemical analysis of the water. For these reasons, laboratory and pilot studies are essential in evaluating the treatability of an unfamiliar water supply or one subjected to a new treatment method (17).

Methods of Removal

The first iron-removal plant was constructed at Charlotten, Germany in 1874. The first plant to remove manganese along with iron was completed in 1889, in Zutphen, Holland. In 1893, the first iron-removal plant in the United States was put into operation at Atlantic Highlands, New Jersey. The earliest plants employed aeration and filtration, sometimes supplemented by the addition of lime (4).

By 1941 there were about 598 iron and manganese removal plants in the United States. The great majority served small communities and the total pumpage was only 220 million gallons per day (mgd) or an average of 370,000 gallons per day (gpd) per plant. Seventeen years later (1958), approximately 1340 water-treatment plants, roughly 14 percent of the total in the United States, included processes for the removal of iron and manganese (4).

Oxidation is generally believed to be the most effective process in removing soluble iron and manganese (18). However, proper treatment of waters containing iron and manganese largely depends upon the exact character of the water (19). Precipitation and agglomeration of iron and manganese during oxidation is not instantaneous. Even where strong oxidants such as chlorine, ozone, and potassium permanganate are used, detention must be provided to allow time for both oxidation reactions to proceed and for oxidized iron and manganese to agglomerate to a size capable of removal by filters (4).

There are a number of techniques employed to accomplish oxidation (20).

1. Aeration
2. Potassium Permanganate
3. Ozone
4. Hypochlorites
5. Chlorine
6. Chlorine Dioxide
7. Catalyst

Other iron and manganese removal methods include:

1. pH adjustment with lime
2. Manganese dioxide

Aeration.

The most commonly-used agent for oxidation of iron and manganese is oxygen. It is added to water through aeration. In practice, aeration may be accomplished by one or more of the following procedures (2).

a) Cascade aerators in which water flows by gravity over trays so that the water droplets are exposed to air. Often the air is forced or induced into the aerator countercurrent to the downward flow of water.

b) Devices which spray the water into the air through nozzles.

c) Diffused aeration in which air is bubbled through the water.

d) Aspirator devices, eg. venturi devices.

Although in many instances aeration is satisfactory, it is often ineffective in bringing about complete oxidation of iron and manganese. Also, when high concentrations of manganese are present, or when the iron and manganese exist as complexes or chelates, air oxidation is generally ineffective (6)(22).

However, aeration is usually effective in oxidizing iron in waters devoid of manganese. The reaction of oxygen with ferrous iron leads to the formation of ferric oxides or hydroxides according to the following equation:

$$Fe(+2) + \frac{1}{4}O_2 + 2OH^- + \frac{1}{2}H_2O \rightarrow Fe(OH)_3\downarrow \qquad (6)$$

Stoichiometrically, 1 mg/l of oxygen will oxidize 7 mg/l of ferrous iron (2).

The oxidation of manganese by air alone is usually a slow process at the pH values generally encountered in practice. To obtain manganese oxidation rates rapid enough to be practical, the pH should be raised to between 9.0 and 10.3. However, aeration is often used as an effective first step in manganese oxidation because it not only adds oxygen to reduce the quantity of oxidizing chemical needed, but also offers an economical means of stripping carbon dioxide and hydrogen sulfide from the water. The increase in pH brought about by the removal of these gases reduces the amount of chemicals needed for pH adjustment (21).

Potassium Permanganate.

It seems paradoxical that a manganese compound would be effective in removing manganese from water. Manganese in the permanganate form is an oxidizing agent which converts dissolved iron and manganese to their insoluble states, making it possible to remove these two elements as precipitates (24). Potassium permanganate ($KMnO_4$) is usually fed continuously to the water that is held for a time in a reaction basin to allow the oxidation reaction to occur. Following the reaction basin the water is filtered through anthracite coal, sand, or a dual-layer bed consisting of anthracite coal underlaid with manganese greensand (19).

The reactions of permanganate with ferrous and manganous ions are: (10)(27)

$$\mathrm{Fe}\ (+2) + \mathrm{MnO}^-_4 + 8\mathrm{H}^+ \rightarrow \mathrm{Mn}(+2) + 5\mathrm{Fe}(+3) + 4\mathrm{H}_2 \qquad (7)$$

and

$$\mathrm{Mn}(+2) + 2\mathrm{MnO}^-_4 + 2\mathrm{H}_2\mathrm{O} \rightarrow 5\mathrm{MnO}_2 + 4\mathrm{H}^+ \qquad (8)$$

Theoretically, one part $KMnO_4$ will oxidize 1.06 parts of soluble ferrous iron to its insoluble ferric state or 0.52 parts of divalent manganese to insoluble tetravalent manganese (18)(20)(23)(24).

Practical experience shows that the theoretical permanganate requirement is usually in excess of the actual amount required to oxidize the iron and manganese. This is attributed to secondary oxidation reactions in which manganese sesquioxide ($Mn_2O_3 \cdot x\ H_2O$) and ferric ions are formed in the reaction with iron: (18)(20)

$$Fe(+2) + Mn_2 \cdot 2H_2O \rightarrow Fe(+3) + Mn_2O_3 \cdot x\ (H_2O) \qquad (9)$$

And, in the reactions with manganese, (22)(26) manganese sesquioxide;

$$Mn(+2) + MnO_2 . 2H_xO \rightarrow Mn_2O_3 . x\ (H_2O) \qquad (10)$$

and mangano-manganic oxide;

$$2\ Mn\ (+2) + MnO_2 . 2H_2O \rightarrow Mn_3O_4 . x\ (H_2O) \qquad (11)$$

or more correctly, $MnO . Mn_2O_3 . x(H_2O)$ is formed. The end products of these secondary oxidations are insoluble. In addition to the secondary reaction, there is also evidence that MnO_2 may act as a catalist, thus increasing the rate at which the redox reactions occur (20). For these reasons, it is necessary to use empirical procedures to determine proper dosages of $KMnO_4$.

Permanganate oxidation generally occurs at a fairly rapid rate. Iron is oxidized almost instantaneously (20) and manganese will oxidize within five minutes at pH values from 5.0 to 9.0 (6). Any additional reaction time allows the oxidized iron and manganese to settle in the reaction basin, thereby relieving the load on the filters. Also, $KMnO_4$ will usually oxidize organically-bound iron and manganese more rapidly than aeration, chlorine, or chlorine dioxide (18). In addition, the reaction of iron and manganese with $KMnO_4$ is not dependent upon pH as with other oxidants.

Potassium permanganate is also effective in removing color, taste and odor from water within the pH limits normally encountered. Also, $KMnO_4$ is an effective algicide and its toxicity to fish is much lower than other agents commonly used for this purpose. As a disinfectant, the action of permanganate surpasses that of chlorine in destroying some viruses. However, the oxidation and disinfection effect of permanganate does not continue through the filters. Therefore, chlorine must be applied following filtration to maintain a free residual of disinfectant. In other words, pre-oxidation with $KMnO_4$ produces a conditioned water in which the addition of chlorine in post treatment accomplishes its job without producing chlorinous odors and tastes (24).

Potassium permanganate may be fed in crystalline form or as a solution. It weighs about 100 pounds per cubic foot of dry chemical, is dustless, safe to handle, and can be kept indefinitely in dry storage. It is odorless, does not produce harmful vapors and can be handled by conventional methods. However, $KMnO_4$ is not compatible with rubber, so pump diaphragms and chemical feed lines should be made of plastic. Metallic pipelines are entirely satisfactory for transporting the permanganate solution (24).

Potassium permanganate has been used for iron and manganese removal in the United States for many years. Its use, as with other methods, should be based on laboratory or pilot-scale experiments and cost comparisons (24). Generally, it is cost effective for waters when the sum of the iron and manganese concentrations does not exceed approximately 15 mg/l (3).

Frequently, pre-oxidation using aeration or pre-chlorination is practiced in conjunction with permanganate treatment. These schemes serve to reduce the permanganate dosage and, in some instances, result in a net reduction in treatment costs.

Ozone.

Although ozone is a more powerful oxidant than permanganate and other oxidants used for iron and manganese removal, no published data could be found comparing its effectiveness, advantages and disadvantages with those of permanganate.

Hypochlorites.

Hypochlorites applied as sodium or calcium salts, hydrolize to hypochlorous acid which is a stronger oxidant than molecular oxygen. Therefore, soluble iron and manganese are more rapidly and completely oxidized by hypochlorites than aeration. However, this process has certain limitations. In most cases dosages higher than the theoretical amount are required. Also, chloro-derivatives of organic compounds can be formed which cause taste and odor problems and have been shown to be carcinogenic in test animals (27). Additionally, hypochlorous acid does not effectively oxidize manganese and organically-bound iron and manganese (20).

Chlorine Gas.

Chlorine, like hypochlorites, first reacts with water forming hypochlorous acid. Therefore, it is subject to the same limitations as hypochlorites (20).

Chlorine Dioxide.

Chlorine Dioxide, formed by reacting sodium chlorite with chlorine, is a strong oxidizing agent which will rapidly oxidize soluble iron and manganese. It is used predominantly to oxidize manganese. However, the cost of chlorine dioxide is generally prohibitive (20).

Catalysis.

A variety of catalysts are available, the most common is the cupperous ion (Copper II). Catalysts are used to enhance air oxidation and is limited in its use (20).

Adjustment of pH.

Adjustment of pH is an effective means of removing iron and manganese in lime or lime-soda softening plants. Generally this gives satisfactory results since the pH range is about 9.5. This process is more efficient when preceded by aeration (20).

Lime precipitates the insoluble ferrous hydroxide in an alkaline medium as follows:

$$\left.\begin{array}{l} FeSO_4 \\ FeCO_3 \\ FeCl_2 \end{array}\right\} + Ca(OH)_2 \rightarrow \left.\begin{array}{l} CaSO_4 \\ CaCO_3 \\ CaCl_2 \end{array}\right\} + Fe(OH)_2\downarrow \qquad (12)$$

where 1 gram of iron corresponds to 1 gram of CaO. However, in an acid or neutral water, the ferrous hydroxide is soluble. So under acid or neutral conditions and the presence of oxygen, the ferrous hydroxide is rapidly converted into ferric hydroxide:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow Fe(OH)_3\downarrow \qquad (13)$$

and 1 gram of iron corresponds to 0.14 grams of oxygen. (2)

This method of treatment was employed for "super high" iron concentrations (64, 110, and 174 mg/l) in Alaskan villages. The finished water quality had iron concentrations within the limits of the USPHS recommendations (26).

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Manganese is readily removed by adding sufficient lime to raise the pH to a range of 9-10 (28). At this pH value manganese is rapidly oxidized by the oxygen dissolved in the water. On the other hand, the raising of alum-treated water to such a high pH range generally results in peptizing a sizable portion of the alum floc carried over from the sedimentation basins. Such peptization results in the passage of alum through the filter, to precipitate later in dead ends of the distribution system. Therefore it can be said that manganese can be removed by conventional treatment plants, but only with some impairment to the quality of the finished water (28). If lime or lime-soda softening is not practiced, pH adjustment for iron and manganese removal is seldom economically feasible (20).

Manganese Dioxide.

Manganese dioxide affixed to a greensand filter media, called manganese greensand, is effective in removing soluble iron and manganese. The greensand filter is regenerated with $KMnO_4$ by either the batch or the continuous flow processes. Iron and manganese removal by this method is sometimes called the manganese zeolite process, although it does not involve ion exchange, rather they are removed by adsorption. The adsorbed iron and manganese are periodically oxidized by dosing the bed with permanganate (29).

METHODS AND MATERIALS

Description of Pilot Plant

The pilot plant used in these studies is shown photographically in Figure 1. This plant consisted of a constant-head tank, counter-current aerator, mixing chamber, upflow basin, and filter. The plant was constructed of non-ferrous materials, mostly aluminum and polyvinylchloride (PVC) to eliminate any possible addition of ferrous ions to the water by corrosion. The constant-head tank is shown in Figure 2. This unit was a 15 cm (6 in) cubical acrylic tank. An overflow spout was located above the bottom of the constant-head tank to maintain the liquid depth at 10.2 cm (4 in). A brass valve was located 2.5 cm (1 in) above the bottom to insure a constant flow of water to the aerator. The constant-head tank was elevated so that the water level was 46 cm (18 in) above the inlet of the aerator.

The aeration unit, depicted in Figure 3, was 15 cm (5.91 in) in diameter and made of Schedule 40 transparent PVC pipe. The aerator design, presented in Appendix I was in accordance with Ten States Standards (30) using 7 trays. The top tray was used to distribute the water evenly over the remaining trays. Each tray was made from 4.8-mm (3/16-in) perforated PVC sheet stock. The trays, held in place by aluminum wires, were removable to facilitate cleaning. A 55-cfm Dayton Box Fan (Model 4C548) manufactured by Dayton Electric Manufacturing Co., was used for aeration. This fan, located at the top of the aerator, induced air entering at the bottom of the aerator to flow upwards and

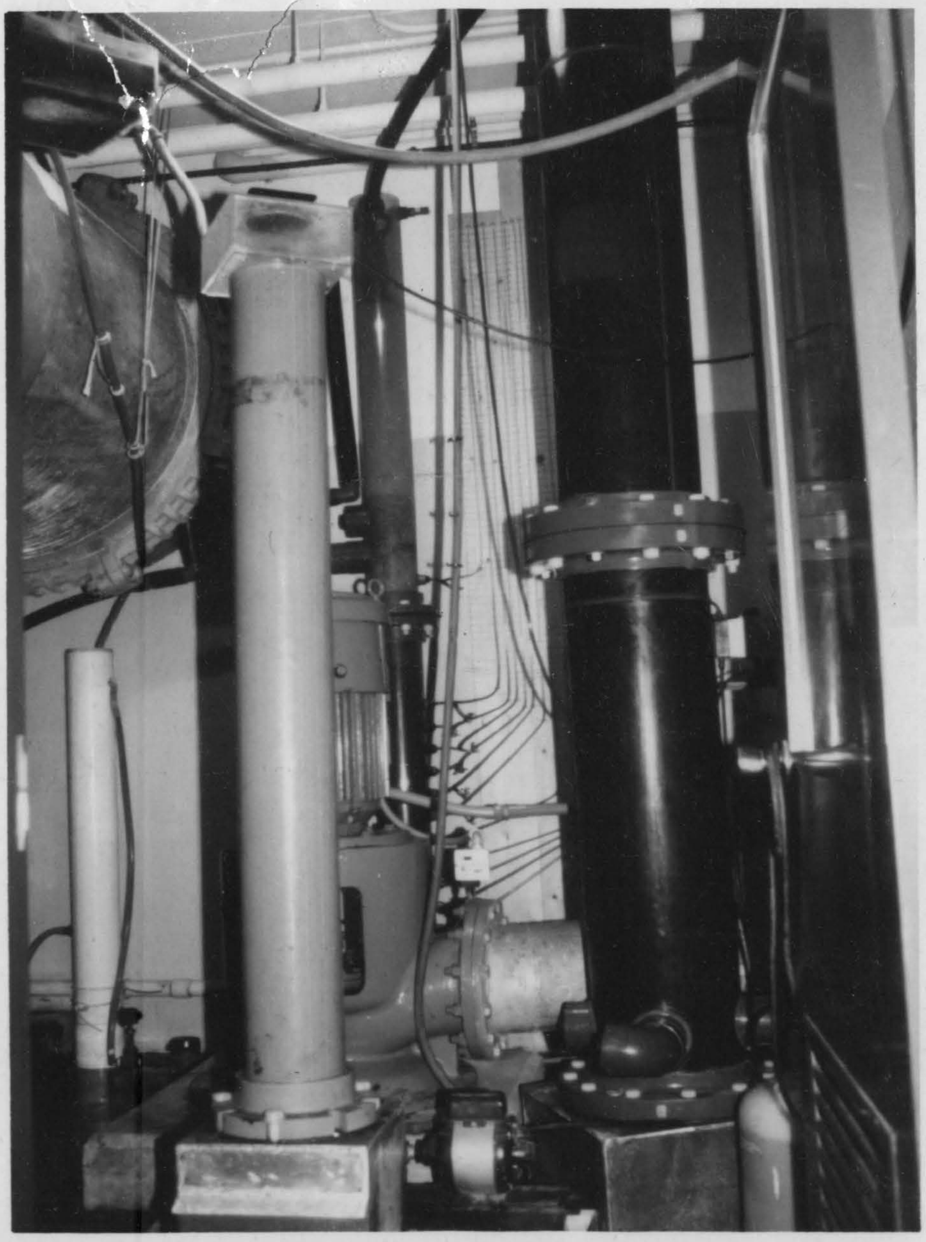

Figure 1. Pilot Set-up. Units from left to right are, Constant head tank (upper left corner), riser tube effluent, aerator, filter and piezometric tubes, and reaction basin.

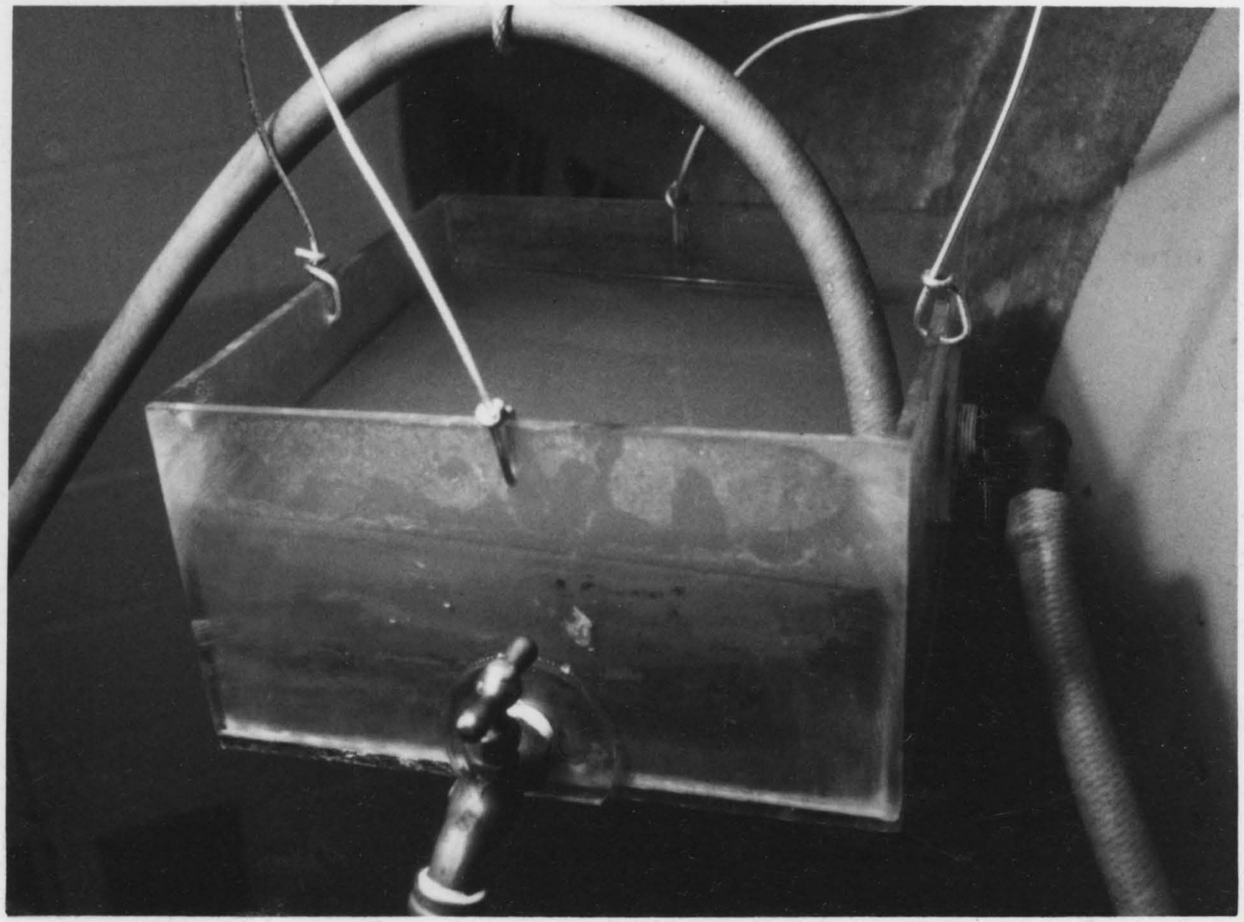

Figure 2. Constant Head Tank.

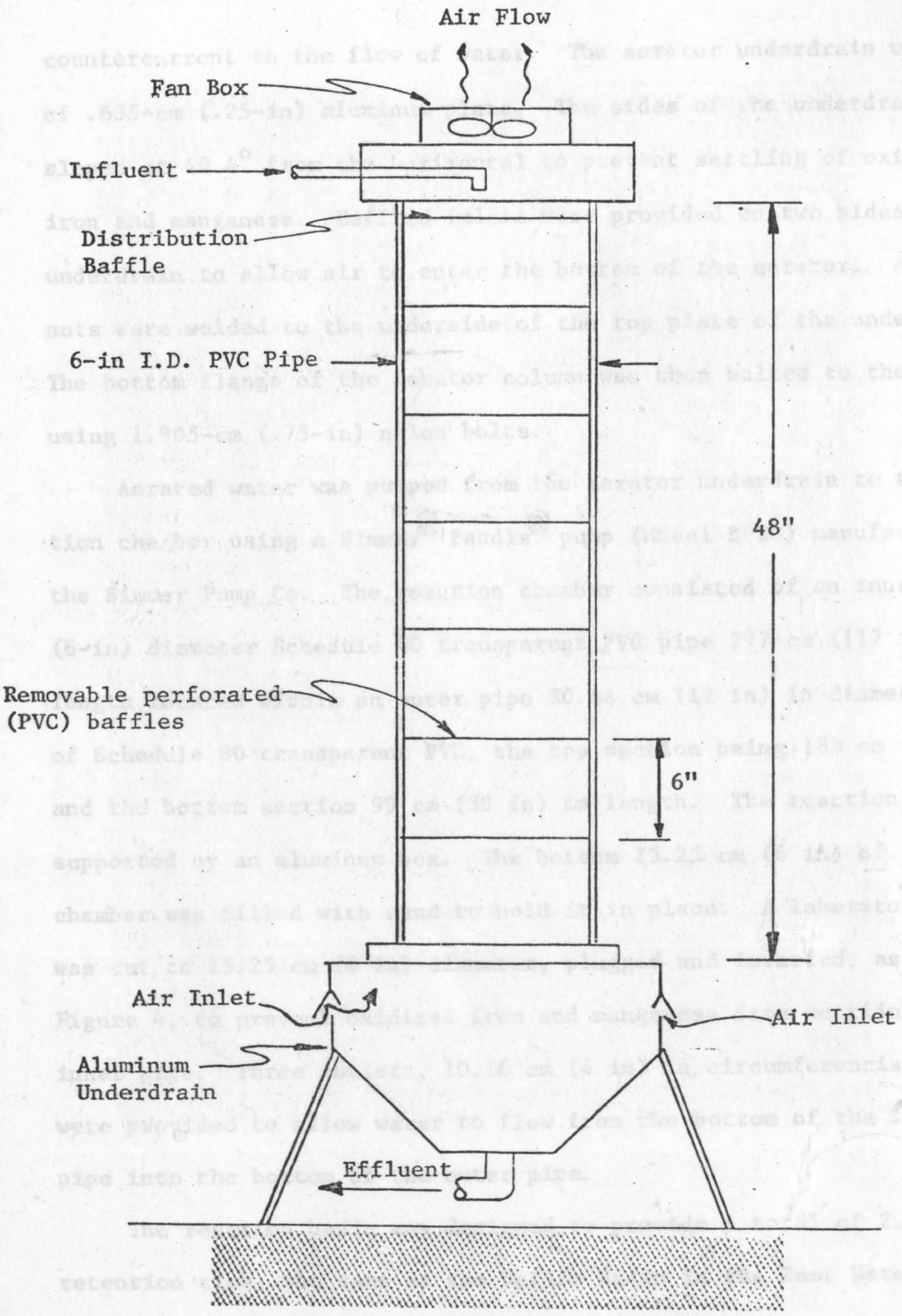

Figure 3. Pilot Aerator

countercurrent to the flow of water. The aerator underdrain was made of .635-cm (.25-in) aluminum plate. The sides of the underdrains were sloped at 48.4° from the horizontal to prevent settling of oxidized iron and manganese. Baffled inlets were provided on two sides of the underdrain to allow air to enter the bottom of the aerator. Aluminum nuts were welded to the underside of the top plate of the underdrain. The bottom flange of the aerator column was then bolted to the underdrain using 1.905-cm (.75-in) nylon bolts.

Aerated water was pumped from the aerator underdrain to the reaction chamber using a Simmer® Paddle® pump (Model BP20) manufactured by the Simmer Pump Co. The reaction chamber consisted of an inner 15.25-cm (6-in) diameter Schedule 40 transparent PVC pipe 297 cm (117 in) in length located within an outer pipe 30.48 cm (12 in) in diameter made of Schedule 80 transparent PVC, the top section being 183 cm (72 in) and the bottom section 99 cm (39 in) in length. The reaction basin was supported by an aluminum box. The bottom 15.25 cm (6 in) of the inner chamber was filled with sand to hold it in place. A laboratory funnel was cut to 15.25 cm (6 in) diameter, plugged and inverted, as shown in Figure 4, to prevent oxidized iron and manganese from settling in the inner pipe. Three outlets, 10.16 cm (4 in) in circumferencial length were provided to allow water to flow from the bottom of the inner pipe into the bottom of the outer pipe.

The reaction basin was designed to provide a total of 2.5 hours retention time, the same as the Upflow Basin in the East Water Treatment

Figure 4. Effluent Ports of Inner Pipe Chamber of Reaction Basin.

Plant. The effluent from the reaction basin was collected at the top in an octagonal-shaped trough and then transferred to the filter unit through PVC piping.

The pilot filter is shown in Figure 5. This unit was made of schedule 80 transparent PVC with a 15.25-cm (6-in) diameter and a height of 2.51 m (99 in). It was divided into two flanged sections. The underdrain for the filter, as pictured in Figure 6, is an aluminum box 23 cm (9 in) in height and 30 cm (12 in) on a side. A 40 cm (16 in) square base plate was welded to the bottom for stability. A removable side was provided to facilitate cleaning of the underdrain. The effluent line from the filter underdrain included valving for backwash, a meter and a plastic effluent riser tube with a diameter of 1.9 cm (.75 in). The riser tube maintained a 4 cm (1.57 in) minimum water depth over the filter media to prevent air binding. The backwash effluent line was located so that a 50 percent filter bed expansion could be obtained if desired.

The filter media and support gravel were the same as used in the East Plant filters. The media consisted of No. 1 anthracite coal ranging from 0.6 to 0.8 mm in size with a uniformity coefficient of 1.75. This layer was 76.2 cm (30 in) in depth. The support gravel was 30-cm (12-in) in depth. Twelve piezometric tubes enabled the measurement of head losses throughout the filter media on 7.5 cm (3 in) centers.

A Wallace Tiernan series 94-100 Chemical feed pump was used to feed potassium permanganate to the reaction basin.

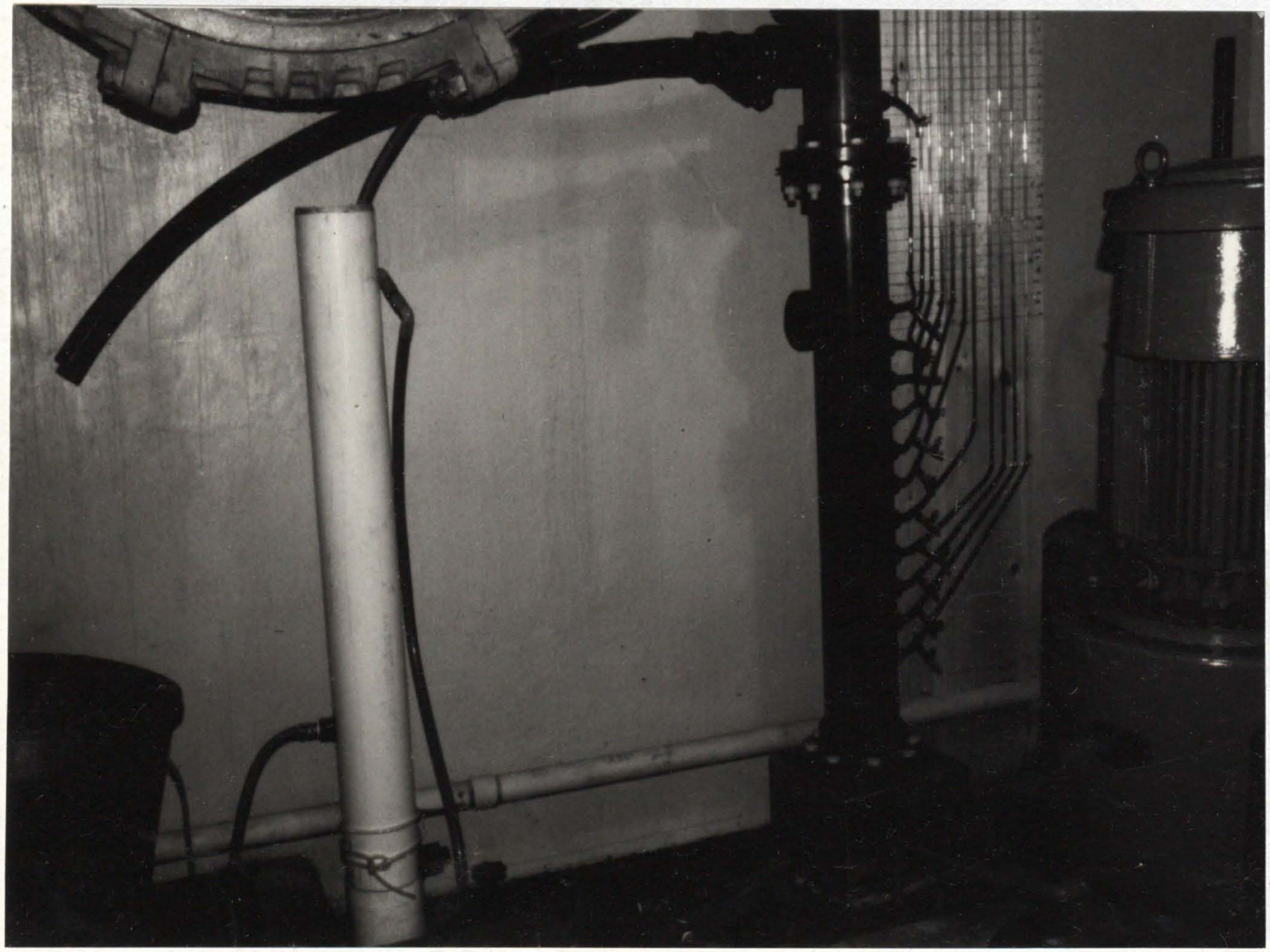

Figure 5. Pilot Filter Set-up.

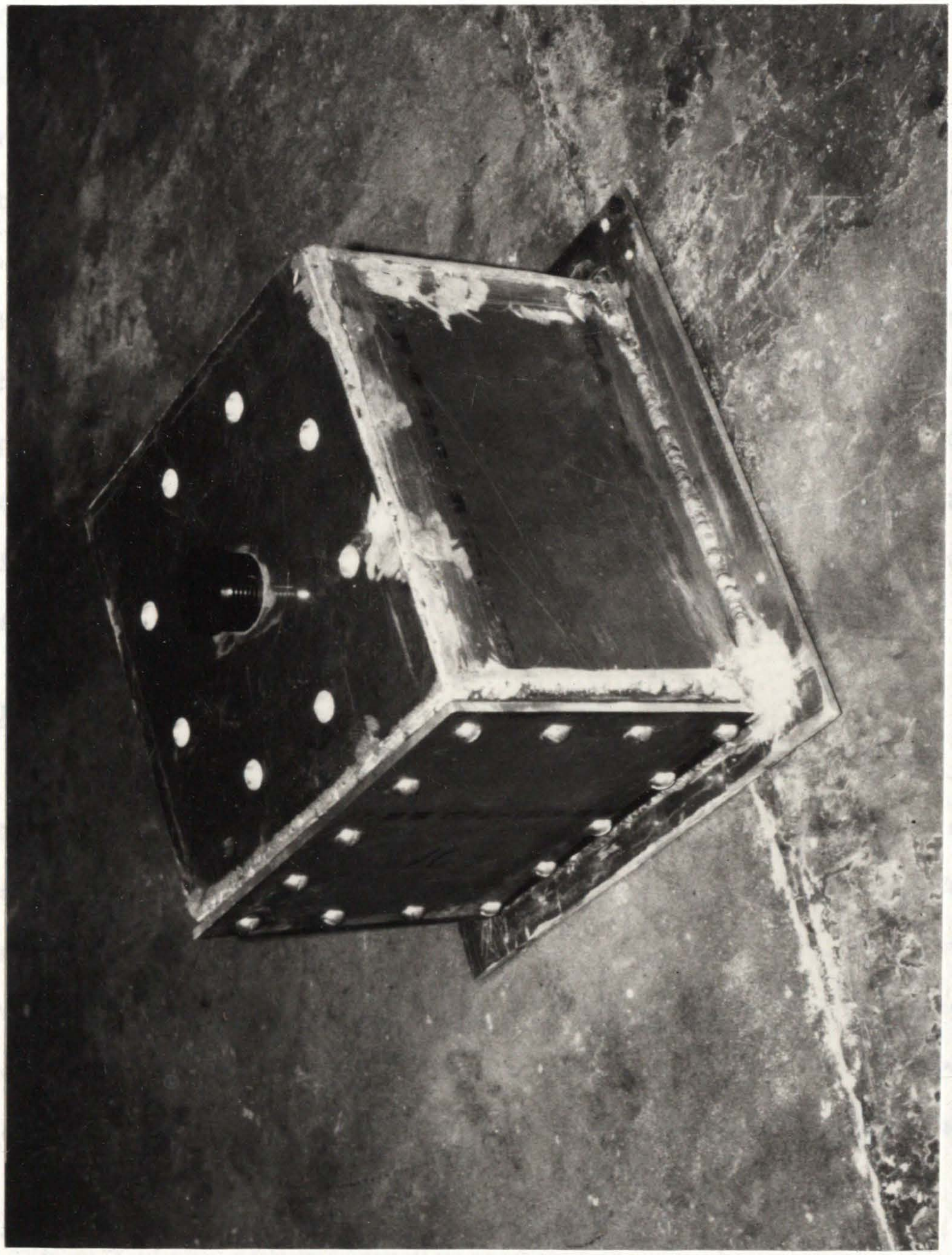

Figure 6. Pilot Filter Underdrain.

Pilot Plant Operation

The pilot plant was first operated on January 5, 1979. Raw water from Well No. 1 was obtained from the influent line entering the East Water Treatment Plant, located east of Interstate Highway 29 in Brookings, South Dakota. Initially, the filter was backwashed for two hours to remove excessive dust and fines from the medium. Backwash water was obtained from the high service pumping station discharge line. Backwash flow was adjusted as needed to provide for 50 percent filter bed expansion. This was done by visual means since the filter was transparent. No ripening period was required since the filter media used was the same as used by Farvardin in 1977-1978 (31). Farvardin ripened the filter for a total of 73 days followed by several months of operation for data collection. The filter rate was 2 gal/min./sq ft.

Length of Filter Runs

Filter runs for both the East Plant and the pilot plant were 48 hours in length. After each run the pilot filter was backwashed for seven minutes. The backwash time was the same as the East Water Treatment Plant. Beginning March 1, 1979, the filters at the East Plant were backwashed when the headloss through the filters reached 8 feet or had operated for 10 days, whichever came first. Pilot operation did not change maintaining continuity throughout the experiments.

Sampling

Samples were collected at 4 locations: 1) from the constant head tank which was considered to be the influent to both the pilot and East

Plant; 2) from the pilot reaction basin effluent; 3) from the pilot plant effluent; and 4) from the clearwell effluent of the East Plant. For each sampling run, two 250-ml samples and one 500-ml sample were collected at each location, except that a 500-ml sample was not taken at the reaction basin effluent. Because manganese has a strong tendency to be absorbed on glass storage bottles (31), plastic containers were used to collect all samples. These samples were analyzed as shown in Figure 7. Temperature, pH, dissolved oxygen, hardness, alkalinity and filtration for soluble iron and manganese determinations were carried out immediately after sampling.

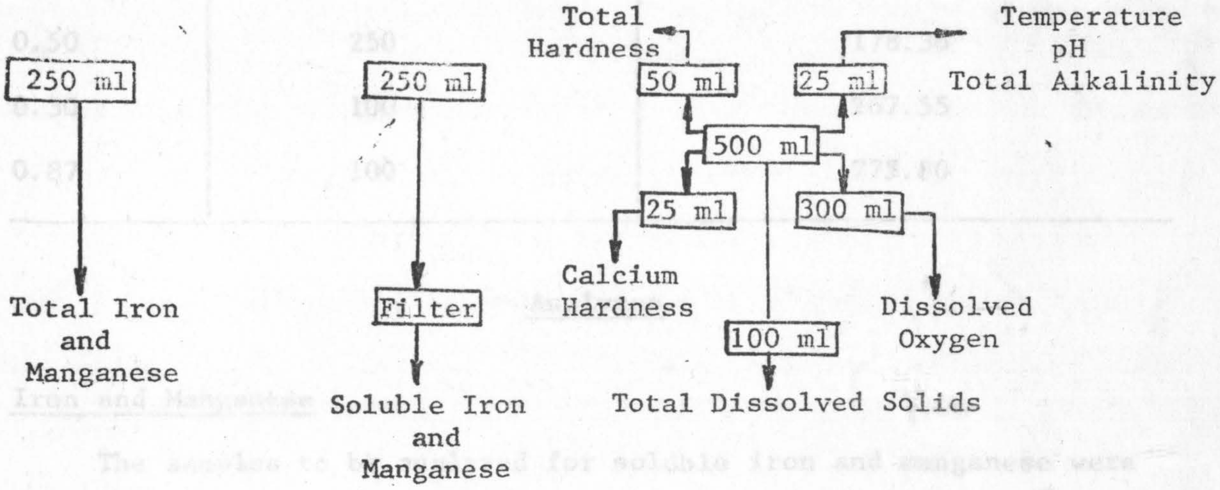

Figure 7. Flow diagram of Chemical Analysis.

Potassium Permanganate Feed

A series of experiments were conducted at different MnO_4^- dosages with at least 96 hours (2 filter runs) of operation at each dosage. Table 3 shows the schedule of operation and MnO_4^- feed concentration. The feed concentrations were varied to enable the feed pump to operate within its normal output range. The feed solutions for the entire study were made by dissolving potassium permanganate crystals in distilled water.

Table 3. Potassium Permanganate Feed Solution Schedule.

	Combination Used	
MnO_4^- Dosage (mg/l)	Feed Solution Concentration (mg/l MnO_4^-)	Feed Rate (ml/hr)
0.0	-	
2.00	250	713.46
1.20	250	428.07
0.50	250	178.36
0.30	100	267.55
0.87	100	775.80

Analyses

Iron and Manganese

The samples to be analyzed for soluble iron and manganese were filtered through a 0.45 micron (μ) membrane filter (Metricel® Membrane Filters manufactured by Gelman Filtration Products) immediately after collection. The first 10 to 25 ml of filtrate were used to rinse the filter flask and were then discarded. The remaining filtrate was saved for analysis. Except for filtration, samples for soluble (filtered) and total (unfiltered) iron and manganese received identical treatment described as follows.

1) Preservation. Each sample was preserved by the addition of 2 to 5 ml of concentrated hydrochloric acid (HCl) to lower the pH to less than 2.0 (32)(33).

2) Concentration. Most samples had iron and manganese concentrations of less than 0.9 mg/l and required concentration. In this procedure a 100-ml sample was evaporated to dryness. Then, approximately 2 ml of 1:1 HCl were used to redissolve the residue. Following this, the contents of the dish were transferred to a 10 ml volumetric flask. The dish was then rinsed using approximately 2 ml demineralized water and 1 ml 1:1 NH_4OH. The ammonium hydroxide (NH_4OH) neutralized the acid. The volume was then brought to 10 ml with demineralized water. Samples having iron and/or manganese concentrations greater than 0.9 mg/l were not concentrated.

3) Analysis. Iron and manganese determinations were made using a Perkin and Elmer 290-B Atomic Absorption Spectrophotometer (Figure 8) with a Jarrel-Ash multi-element neon gas-filled hollow cathode tube. The operating conditions for this instrument during analysis are summarized in Table 4.

Table 4. Operating Conditions of Perkin-Elmer 290-B Atomic Absorption Spectrophotometer for Iron and Manganese Determination.

Metal	Wave Length (nm)	Instrument Setting	Slit Setting (nm)	Light Source	Flame Type
Iron	248.3	144	0.2	Hollow Cathode Lamp (multi-element)	Air-Acetylene oxidizing
Manganese	279.5	199	0.2	Hollow Cathode Lamp (multi-element)	Air-Acetylene oxidizing

Figure 8. Perkin-Elmer 290-B Atomic Absorption Spectrophotometer with Sampler and recorder.

A Technicon Auto Analyzer sampler was used to provide an equal aspirating period for each sample. The output was recorded as relative absorbance on a Moseley 680 Strip-Chart Recorder manufactured by Hewlett-Packard.

Stock solutions for the iron and manganese analysis were prepared in accordance with Standard Methods (33). Each stock solution was then diluted to a metal concentration of 100 mg/l from which the standards were prepared. Standards of 0.0, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 mg/l of iron and manganese were prepared. Since iron and manganese co-exist naturally in raw water entering the Brookings East Plant, the standard solutions were combined into one solution containing equivalent concentrations of iron and manganese.

The standard curve is a straight-line relationship between the metal concentration and the measured relative absorbance. Concentrations of iron and manganese in the concentrated samples (unknowns) could be measured to the nearest 0.01 mg/l (10 μg/l) iron and/or manganese. Unconcentrated samples could be measured to the nearest 0.1 mg/l (100 μg/l) (32).

pH

Measurement of pH was made using a Corning 610 portable pH meter equipped with glass and calomel electrodes. The pH of the samples was taken within 30 minutes after sample collection. The pH was measured prior to the total alkalinity analysis. The pH meter was standardized twice daily, once prior to analysis and once upon completion of all analytical work for the day.

Temperature

The temperature of the samples was taken with a thermometer immediately following collection. The temperature was taken of all samples except the reaction basin effluent.

Total Hardness

The UniVer II titration method by HACH Chemical Company (34) was used to determine total hardness. To conserve titrant, a 25-ml sample was diluted with 25 ml of demineralized water. The 1.0-gm scoop of UniVer II Powder was used instead of the UniVer II Powder Pillow. EDTA (.0200N) was used as titrant instead of HACH's TitraVer.

Calcium Hardness

The Hach procedure was also used to determine calcium hardness (34). A 0.1-gm scoop of CalVer II Powder was substituted for the CalVer II Powder Pillow. EDTA (.0200N) was used as titrant instead of the HACH equivalent TitraVer.

Alkalinity

Alkalinity was determined by potentiometric titration to a preselected pH as described in Standard Methods (33). A 50-ml sample was titrated to a pH of 4.5 and the results reported as mg/l as $CaCO_3$.

Total Residue

Total residue determinations were conducted in accordance with Standard Methods (33). Prior to solids determination, the water samples were stored in sealed plastic containers at 4°C and mixed thoroughly before pipeting to the evaporation dish. Upon evaporation of the 100-ml sample, the dish was transferred to a 103°C oven to obtain a constant weight. The sample dish was dried a minimum of 24 hours to eliminate checking for constant weight which normally can be achieved in 2 to 4 hours. The dish was then cooled in a desiccator at least 60 minutes before final weighing (35).

Dissolved Oxygen

Dissolved oxygen analysis was conducted in accordance with the Idometric Method, Azide Modification as described in Standard Methods (33) except that phenylarsine oxide (PAO) (.0250N), manufactured by HACH Chemical Company, was substituted for sodium thiosulfate. PAO solution is more stable than sodium thiosulfate solution prepared according to Standard Methods and is not affected by bacterial action (34).

Water Stability

Water stability was determined by use of the Lawrence-Caldwell (C-L) diagrams (36). The parameters required for selection of the proper Lawrence-Caldwell diagram are temperature (^{o}C), total dissolved solids and ionic strength. Total residue was used as an approximation of total dissolved solids. This substitution was possible because of the low turbidity of the waters analyzed, the majority of suspended material being oxidized iron and manganese in concentrations of less than 3.0 mg/l.

Ionic strength was estimated using an expression developed by Lowenthal and Marias (37):

$$u = 2.5 \times 10^{-5} S_D \qquad (14)$$

where: u = ionic strength in moles/liter

S_D = total dissolved solids, mg/l

Using mean values for temperature and total residue of the influent and effluent flows, the respective ionic strengths were calculated using Equation 14. These values are shown in Table 5. Lawrence-Caldwell diagrams nearest in temperature and ionic strength to those obtained for the test waters were selected for use from available literature. These diagrams may be found in Appendix II. Although the diagrams selected were derived for temperatures and ionic strengths differing somewhat from the test waters, the estimates of water stabilities obtained using these diagrams are believed to be reasonably valid.

Table 5. Schedule for Lawrence-Caldwell Diagram Usage

Sample		Raw Water	Pilot Effluent	East Plant Effluent
Mean Temperature °C		9.0	12.3	9.0
Mean Total Residue mg/l		660	640	530
Ionic Strength moles/l		.0165	.0160	.0133
Lawrence-Caldwell Diagram Used	Temperature °C	9.0	15.0	10.0
	Ionic Strength moles/l	720	600	600
	Total Residue mg/l	.0180	.0150	.0150
	Reference	3	4	4

To determine the stability, three additional parameters are needed: calcium hardness, alkalinity, and pH. These values when plotted, define a three-sided envelope on the C-L diagram. For example, the envelope obtained for a water having a calcium hardness as 290 mg/l as $CaCO_3$, alkalinity as 260 mg/l as $CaCO_3$, and the pH of 7.85 is shown in Figure 9 (27). The fact that the water described in Figure 9 defines an envelope

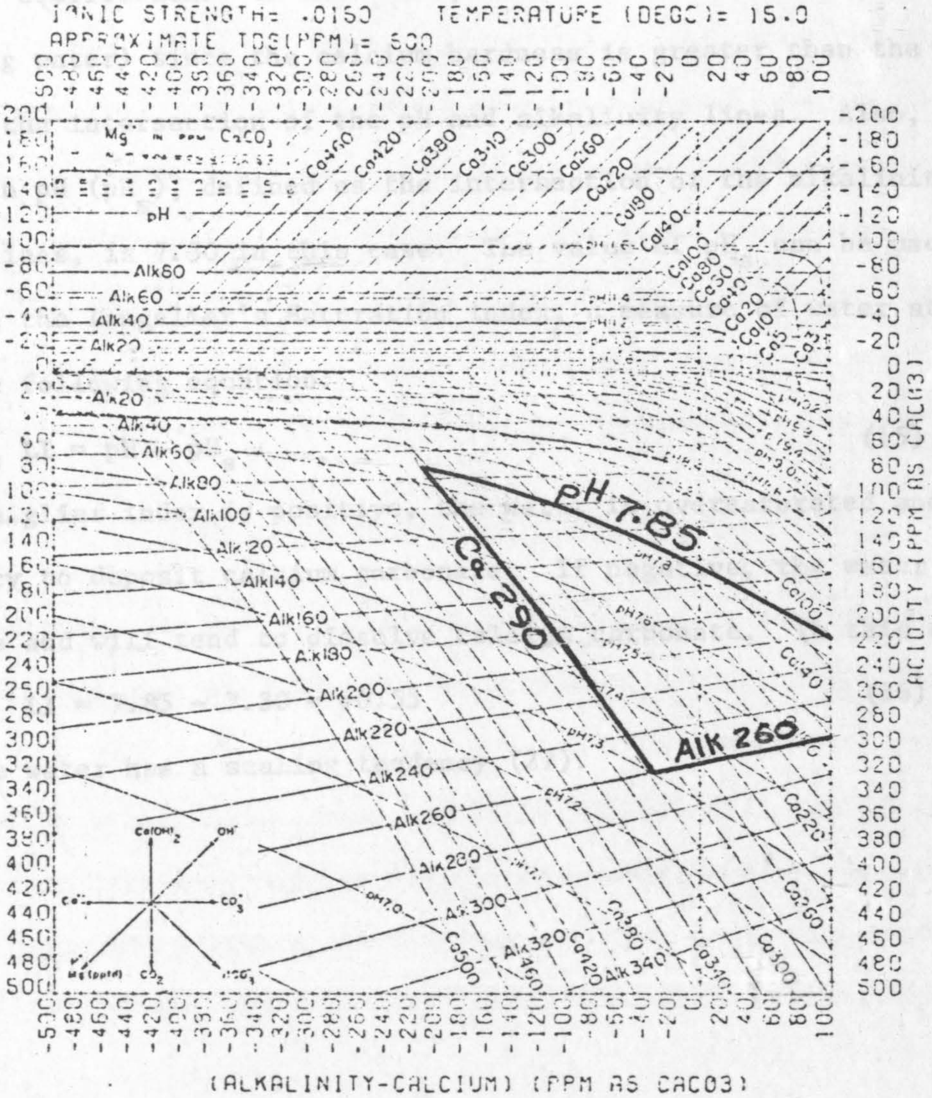

Figure 9. Caldwell-Lawrence Diagram Method of Calculating Water Stability. (35)

rather than a single point indicates that the water is not in calcium carbonate equilibrium. In this case, the water is oversaturated (an encrusting water) since the calcium hardness is greater than the calcium value at the intersection of the pH and alkalinity lines. Also, the saturation pH (pH_s), defined as the intersection of the alkalinity and calcium lines, is 7.30 in this case. The value of pH_s can be used to determine the Langelier's Saturation index, a measure of water stability, using the following equation:

$$LI = pH - pH_s \tag{15}$$

If the Langlier index is positive, the water is oversaturated and has a tendency to deposit calcium carbonate. If negative, the water is corrosive and will tend to dissolve calcium carbonate. In this example:

$$LI = 7.85 - 7.30 = +0.55 \tag{16}$$

thus, the water has a scaling tendency (27).

RESULTS AND DISCUSSION

The major objective of this research was to determine the practicality of removing iron and manganese from a selected water supply at Brookings, South Dakota by the use of aeration and permanganate as oxidants. Soluble and insoluble iron and manganese were measured to determine the removals through the reaction basin and filter. Tests were also performed to determine the stability of the treated effluent. The data collected during the experiment are presented in Appendix III.

Overall Treatment Effectiveness

In general, the use of potassium permanganate to supplement oxidation by aeration was not effective in producing a treated effluent within the limits (0.3 mg/l for iron and 0.05 mg/l for manganese) recommended by the United States Public Health Service (USPHS) (1). As is shown in Figure 10, in only one instance was the pilot effluent in compliance with the recommended limits and that was for iron while the pilot unit was operating in the "aeration only" mode, i.e. without any permanganate feed.

Treatment Unit Performances

The use of potassium permanganate was not successful in providing a treated effluent of acceptable quality on the basis of iron and manganese concentrations. In an attempt to explain this failure, the performance of the treatment units following aeration and the addition of permanganate were evaluated. These units were respectively the reaction basin and filter.

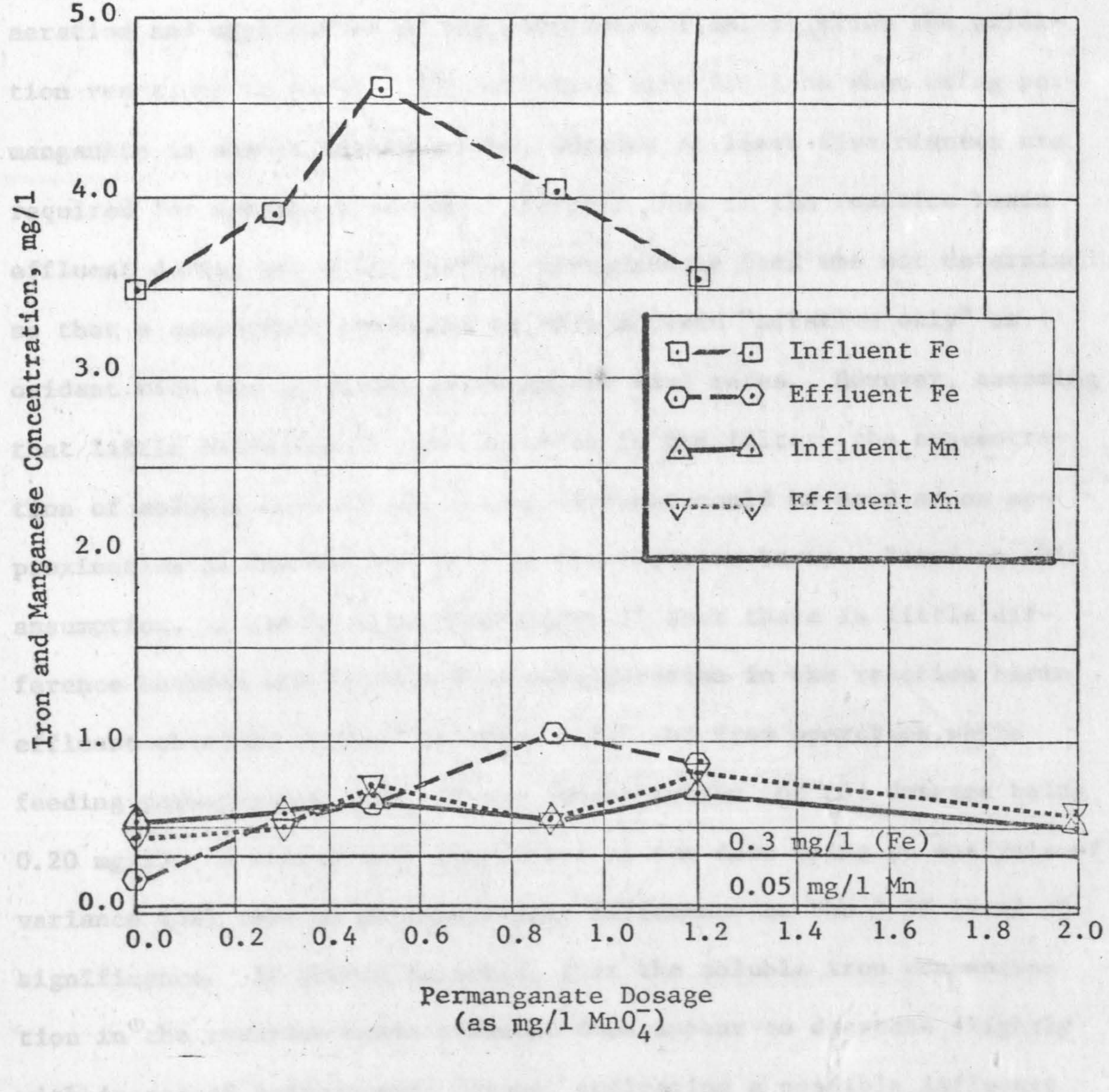

Figure 10. Overall Treatment Effectiveness of Pilot Unit.

Reaction Basin

The primary purpose of the reaction basin in iron and manganese removal by oxidation is to retain the flow for an hour or two after aeration and application of any chemical oxidant to allow the oxidation reactions to occur. The oxidation rate for iron when using permanganate is almost instantaneous, whereas at least five minutes are required for manganese (6)(18). Ferrous iron in the reaction basin effluent during operation without permanganate feed was not determined so that a comparison could not be made between "aeration only" as oxidant with the different permanganate feed rates. However, assuming that little oxidation of iron occurred in the filter, the concentration of soluble iron in the filter effluent could be used as an approximation of the soluble iron in the reaction basin. Based on this assumption, it can be seen from Figure 11 that there is little difference between the soluble iron concentration in the reaction basin effluent obtained during "aeration only" and from operation while feeding permanganate (the average concentration for all dosages being 0.20 mg/l). A statistical comparison of the data using an analysis of variance (38) reveals no significant difference at the 0.50 level of significance. It should be noted, that the soluble iron concentration in the reaction basin effluent does appear to decrease slightly with increased permanganate dosage, indicating a possible influence from this oxidant. However, even if reaction time is also dependent upon the physical and chemical factors listed in Table 2, the design of the reaction basin is usually based upon the time required

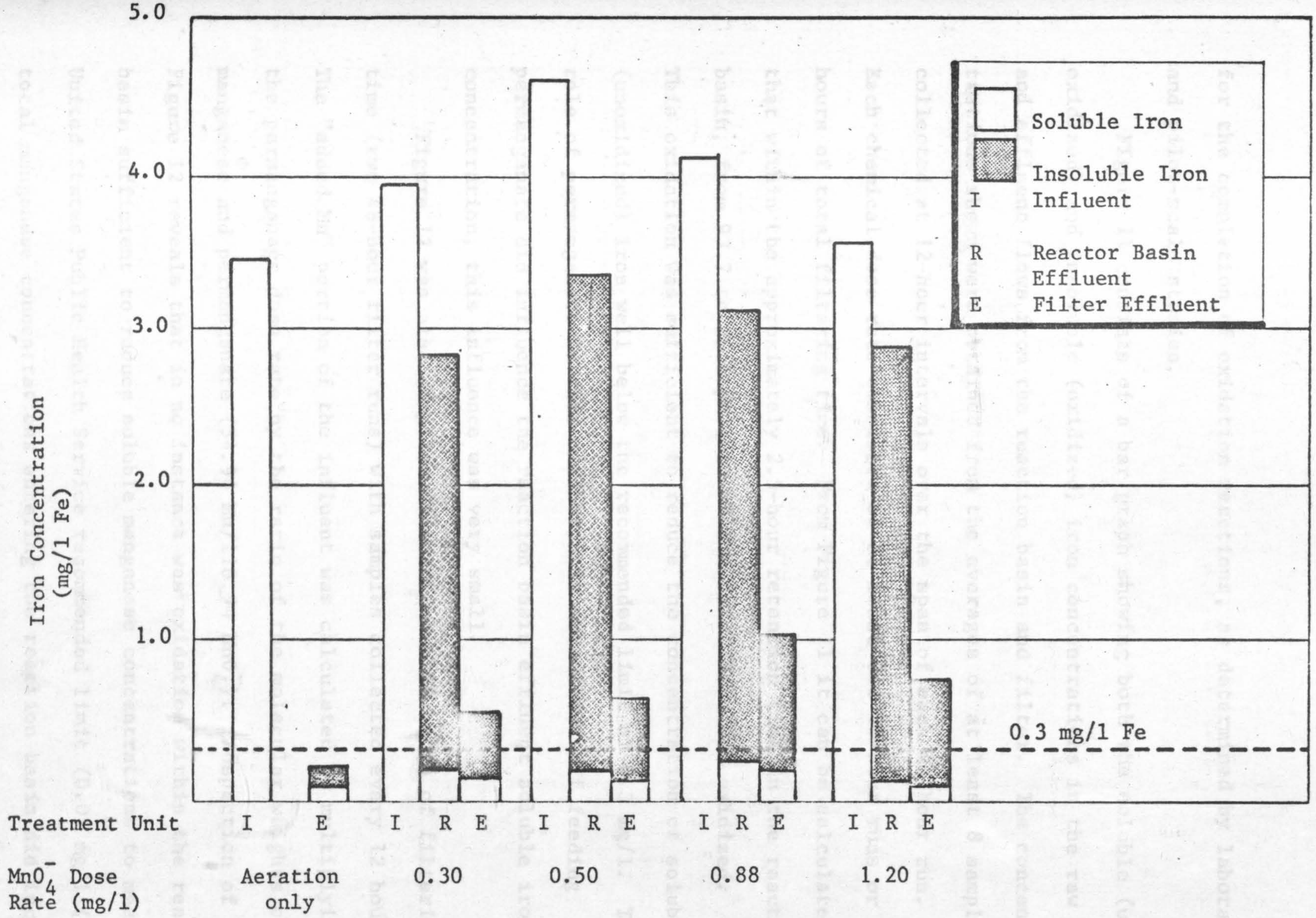

Figure 11. Relationship Between Ferrous and Ferric Iron and MnO_4^- Dosage.

for the completion of oxidation reactions, as determined by laboratory and pilot-scale studies.

Figure 11 consists of a bar graph showing both the soluble (unoxidized) and insoluble (oxidized) iron concentrations in the raw and effluent flows from the reaction basin and filter. The concentrations shown were obtained from the averages of at least 8 samples collected at 12-hour intervals over the span of each 48-hour run. Each chemical dose rate consisted of at least two 48-hour runs or 96 hours of total filtering time. From Figure 11 it can be calculated that within the approximately 2.5-hour retention time in the reaction basin, from 93.7 to 96.6 percent of the total iron was oxidized. This oxidation was sufficient to reduce the concentration of soluble (unoxidized) iron well below the recommended limit of 0.3 mg/l. The role of permanganate in this oxidation is not clear. If feeding permanganate did influence the reaction basin effluent soluble iron concentration, this influence was very small.

Figure 12 was also compiled from at least 96 hours of filtering time (two 48-hour filter runs) with samples collected every 12 hours. The "added Mn" portion of the influent was calculated by multiplying the permanganage dose rate by the ratio of the molecular weights of manganese and permanganate (54.94 Mn/118.94 MnO_4^-). Inspection of Figure 12 reveals that in no instance was oxidation within the reaction basin sufficient to reduce soluble manganese concentrations to meet the United States Public Health Service recommended limit (0.05 mg/l (1). The total manganese concentrations entering the reaction basin did increase

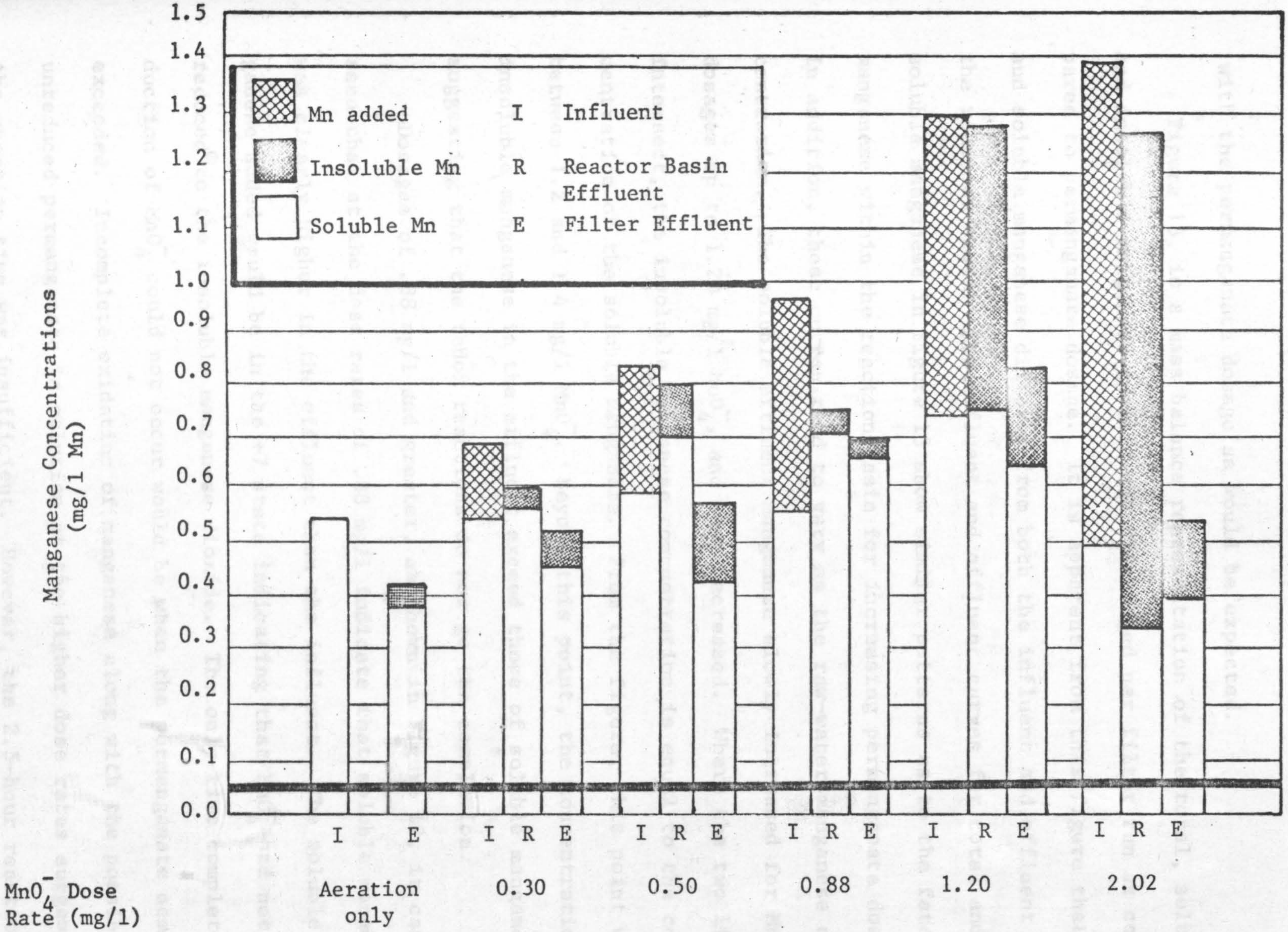

Figure 12. Comparison of Soluble and Insoluble Manganese Versus Permanganate Dosage.

with the permanganate dosage as would be expected.

Figure 13, is a mass balance representation of the total, soluble and insoluble manganese applied and discharged per filter run as compared to permanganate dosage. It is apparent from this figure that total and soluble manganese differed from both the influent and effluent for the reaction basin. The influent and effluent curves for total and insoluble manganese in Figure 13 show similar patterns as to the fate of manganese within the reaction basin for increasing permanganate dosage. In addition, these curves tend to vary as the raw-water manganese concentration. The soluble effluent manganese slowly increased for MnO_4^- dosages up to 1.20 mg/l MnO_4^-, and then decreased. Where the two lines intersect, the insoluble manganese concentration is equal to the concentration of the soluble manganese. From the figure, this point was between 1.2 and 1.4 mg/l MnO_4^-. Beyond this point, the concentrations of insoluble manganese in the effluent exceed those of soluble manganese suggesting that the redox reactions do not go the completion.

Dosages of .88 mg/l and greater, as shown in Figure 12, it can be seen that at the dose rates of .88 mg/l indicate that soluble manganese was clearly higher in the effluent than the influent. The soluble manganese added would be in the +7 state indicating that MnO_4^- had not been reduced to the insoluble manganese dioxide. The only time complete reduction of MnO_4^- could not occur would be when the permanganate demand was exceeded. Incomplete oxidation of manganese along with the possibility of unreduced permanganate in solution at the higher dose rates suggests that the reaction time was insufficient. However, the 2.5-hour reaction time

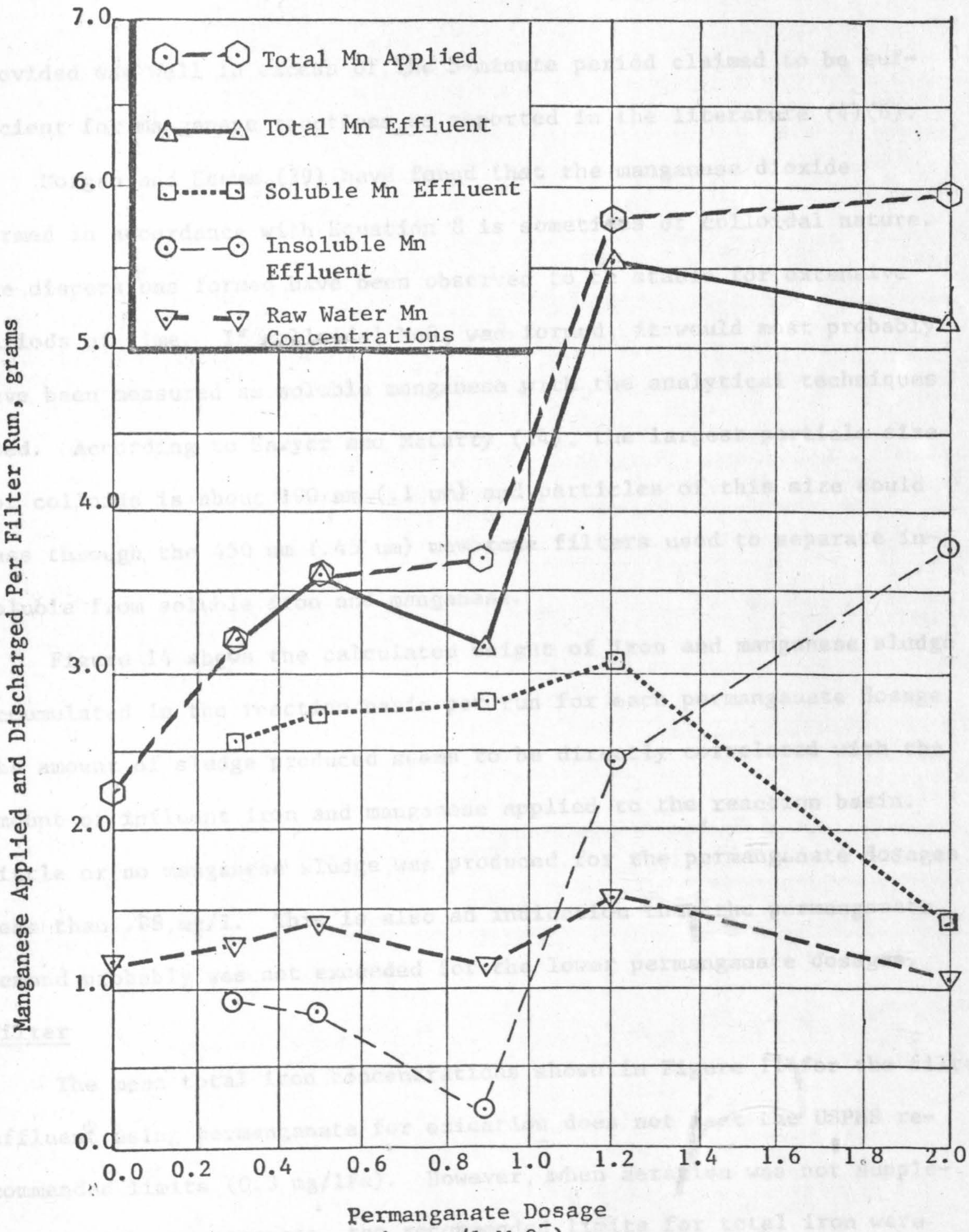

Figure 13. Efficiency of Reactor Basin.

provided was well in excess of the 5-minute period claimed to be sufficient for manganese reactions as reported in the literature (4)(6).

Morgan and Stumm (39) have found that the manganese dioxide formed in accordance with Equation 8 is sometimes of colloidal nature. The dispersions formed have been observed to be stable for extensive periods of time. If colloidal MnO_2 was formed, it would most probably have been measured as soluble manganese with the analytical techniques used. According to Sawyer and McCarty (14), the largest particle size for colloids is about 100 nm (.1 um) and particles of this size could pass through the 450 nm (.45 um) membrane filters used to separate insoluble from soluble iron and manganese.

Figure 14 shows the calculated weight of iron and manganese sludge accumulated in the reaction basin per run for each permanganate dosage. The amount of sludge produced seems to be directly correlated with the amount of influent iron and manganese applied to the reaction basin. Little or no manganese sludge was produced for the permanganate dosages less than .88 mg/l. This is also an indication that the permanganate demand probably was not exceeded for the lower permanganate dosages.

Filter

The mean total iron concentrations shown in Figure 11 for the filter effluent using permanganate for oxidation does not meet the USPHS recommended limits (0.3 mg/lFe). However, when aeration was not supplemented with permanganate, the recommended limits for total iron were met. At all permanganate dosages applied, the soluble iron concentration was greater in the reaction basin effluent than in the filter effluent.

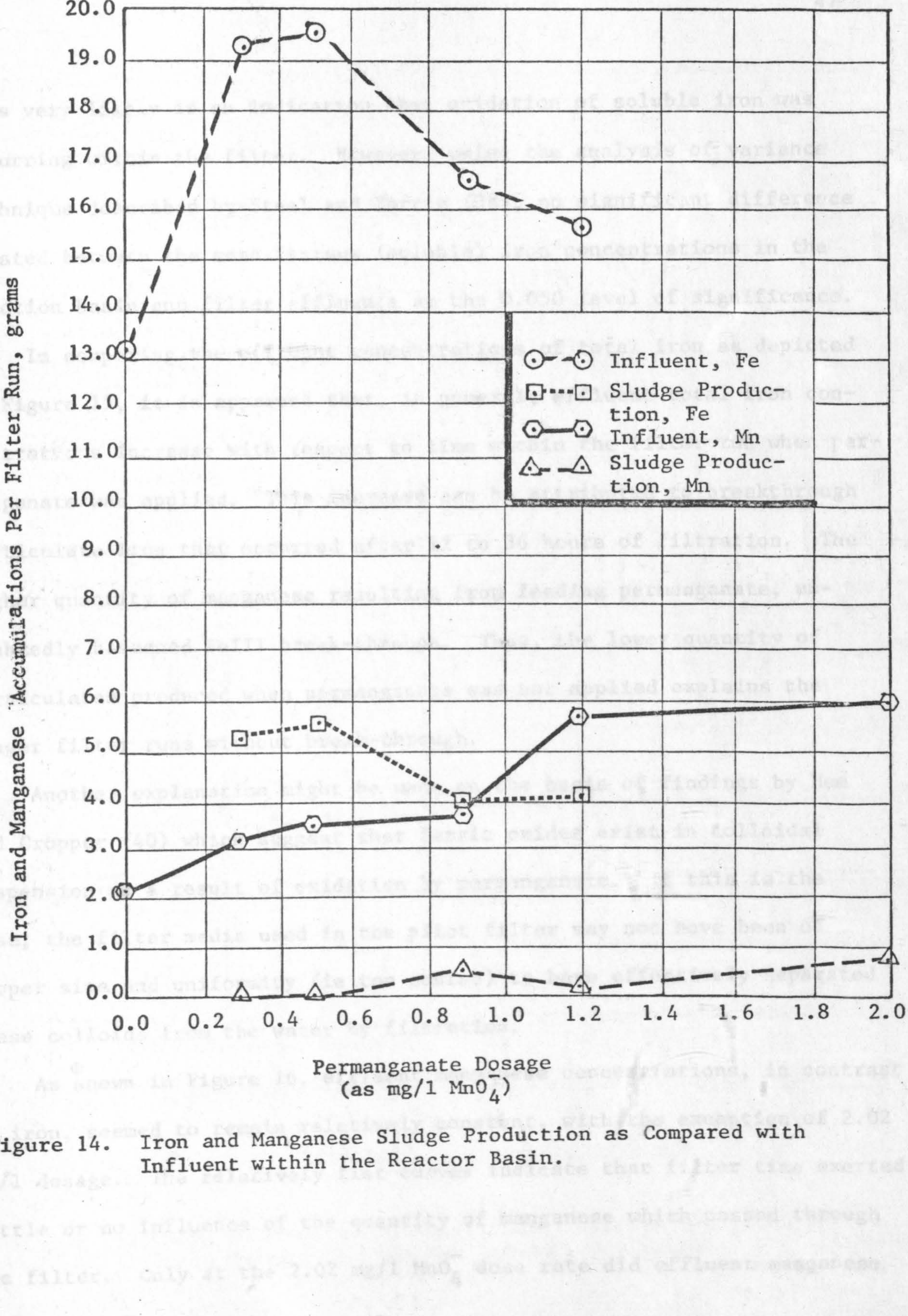

Figure 14. Iron and Manganese Sludge Production as Compared with Influent within the Reactor Basin.

This very likely is an indication that oxidation of soluble iron was occurring within the filter. However, using the analysis of variance technique described by Steel and Torrie (38), no significant difference existed between the mean ferrous (soluble) iron concentrations in the reaction basin and filter effluents at the 0.050 level of significance.

In comparing the effluent concentrations of total iron as depicted in Figure 15, it is apparent that, in general, effluent total iron concentrations increase with respect to time within the filter run when permanganate was applied. This increase can be attributed to breakthrough particulate iron that occurred after 12 to 36 hours of filtration. The higher quantity of manganese resulting from feeding permanganate, undoubtedly hastened FeIII break-through. Thus, the lower quantity of particulates produced when permanganate was not applied explains the longer filter runs without break-through.

Another explanation might be made on the basis of findings by Hem and Cropper (40) which suggest that ferric oxides exist in colloidal suspension as a result of oxidation by permanganate. If this is the case, the filter media used in the pilot filter may not have been of proper size and uniformity (ie too coarse) to have effectively separated these colloids from the water by filtration.

As shown in Figure 16, effluent manganese concentrations, in contrast to iron, seemed to remain relatively constant, with the exception of 2.02 mg/l dosage. The relatively flat curves indicate that filter time exerted little or no influence of the quantity of manganese which passed through the filter. Only at the 2.02 mg/l MnO_4^- dose rate did effluent manganese

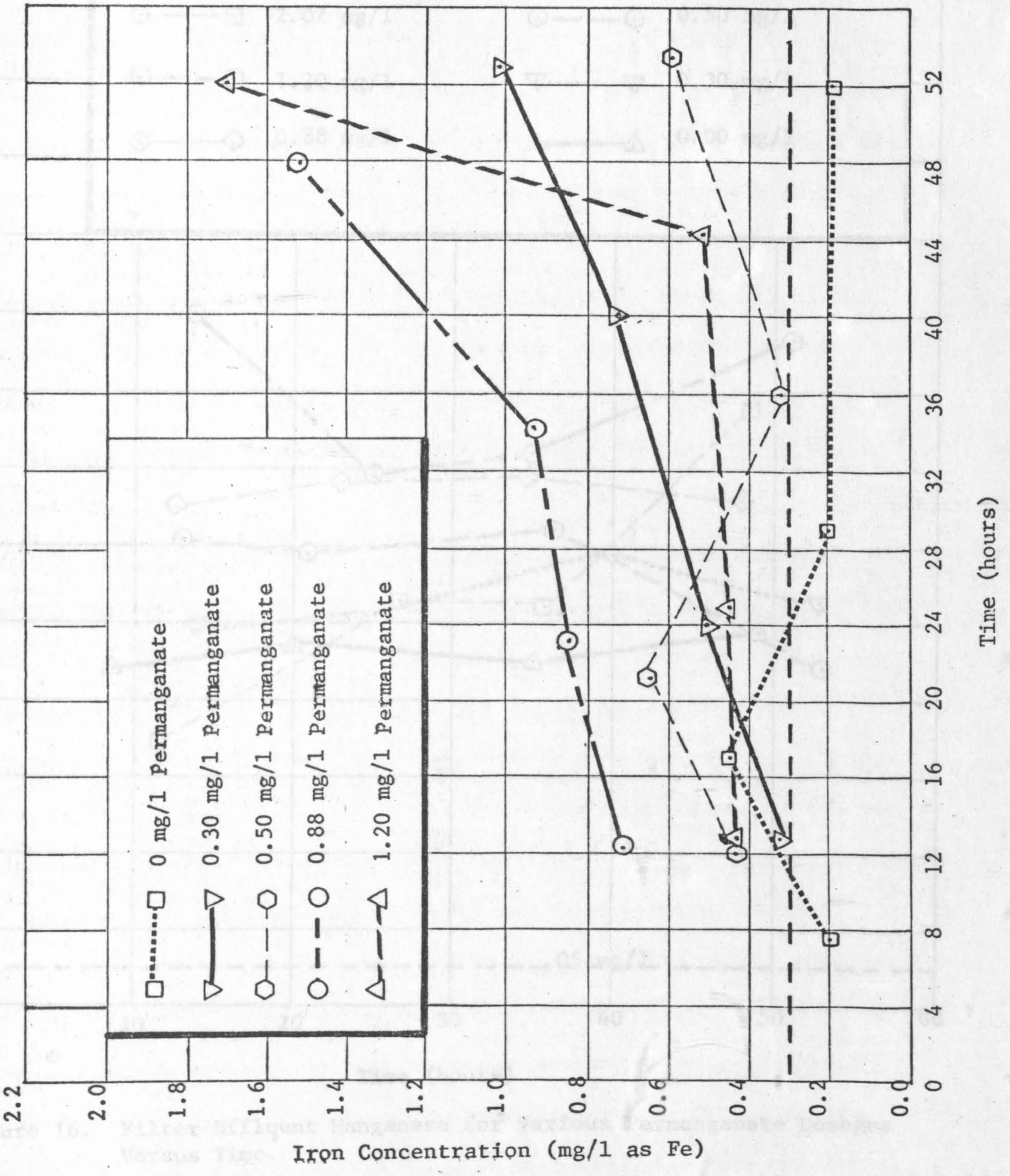

Figure 15. Mean Iron Concentrations Passing Through The Pilot Filter With Respect To Time For Permanganate Dosages.

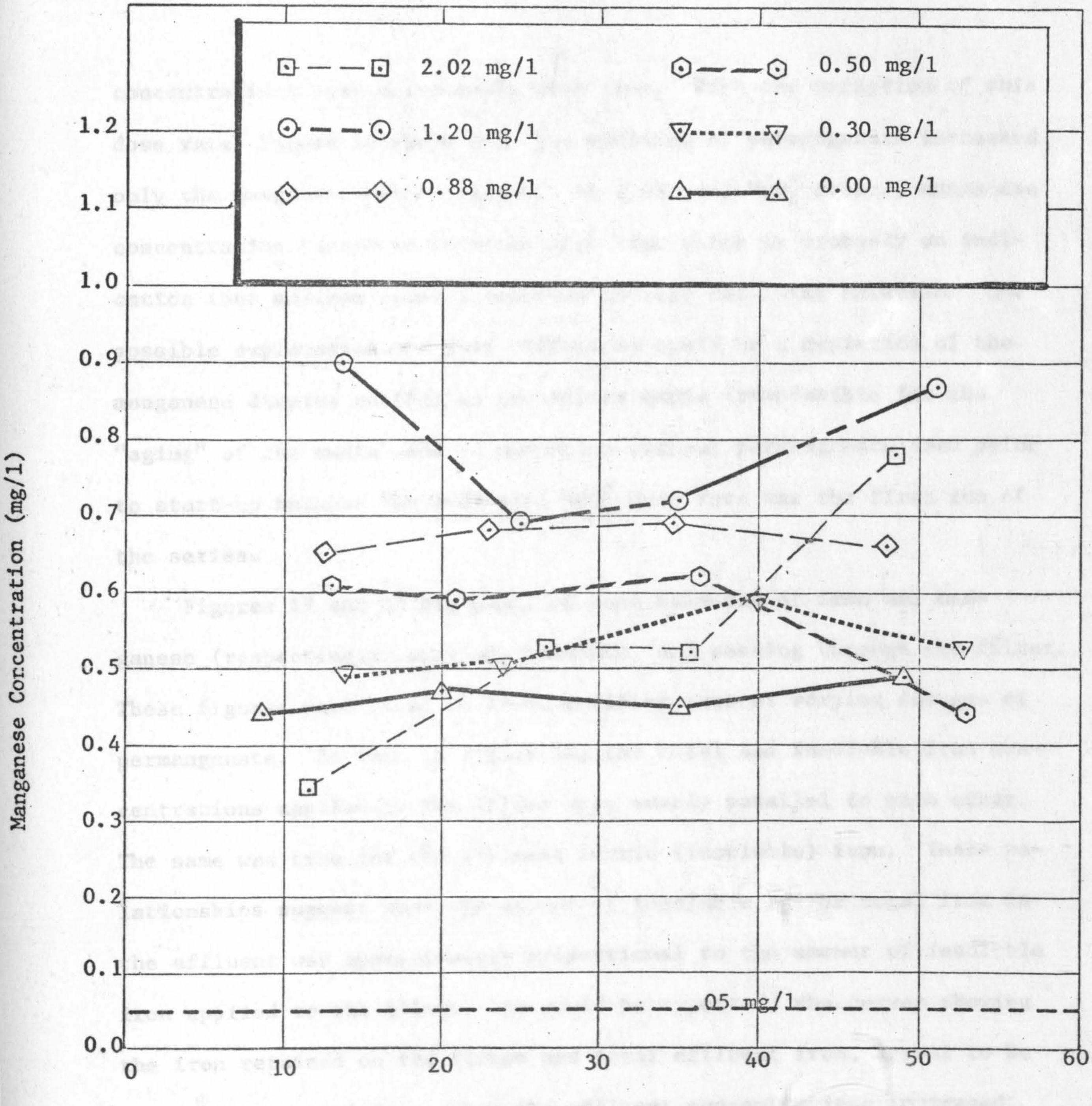

Figure 16. Filter Effluent Manganese for Various Permanganate Dosages Versus Time.

concentrations vary appreciably with time. With the exception of this dose rate, Figure 16 shows that the addition of permanganate increased only the manganese concentration. At 2.02 mg/l MnO_4^- dosage, manganese concentration tended to increase with time which is probably an indication that maximum removal occurred shortly following backwash. One possible explanation for this difference could be a depletion of the manganese dioxide coating on the filter media (responsible for the "aging" of the media) due to operation without permanganate feed prior to start-up because the 2.02 mg/l MnO_4^- dose rate was the first run of the series.

Figures 17 and 18 are plots of mass balances of iron and manganese (respectively) applied, retained, and passing through the filter. These figures were based on 48-hour filter runs at varying dosages of permanganate. As seen in Figure 17, the total and insoluble iron concentrations applied to the filter were nearly parallel to each other. The same was true for the effluent ferric (insoluble) iron. These relationships suggest that the amount of insoluble and/or total iron in the effluent was approximately proportional to the amount of insoluble iron applied to the filter. As would be expected, the curves showing the iron retained on the filter and total effluent iron, appear to be inversely proportional. When the effluent concentrations increased, the amount of iron retained on the filter decreased. It can also be seen in Figure 17 that only minor oxidation occurred within the filter.

In general, soluble iron concentrations were less than the USPHS recommendations. However, because of the insoluble iron passing the

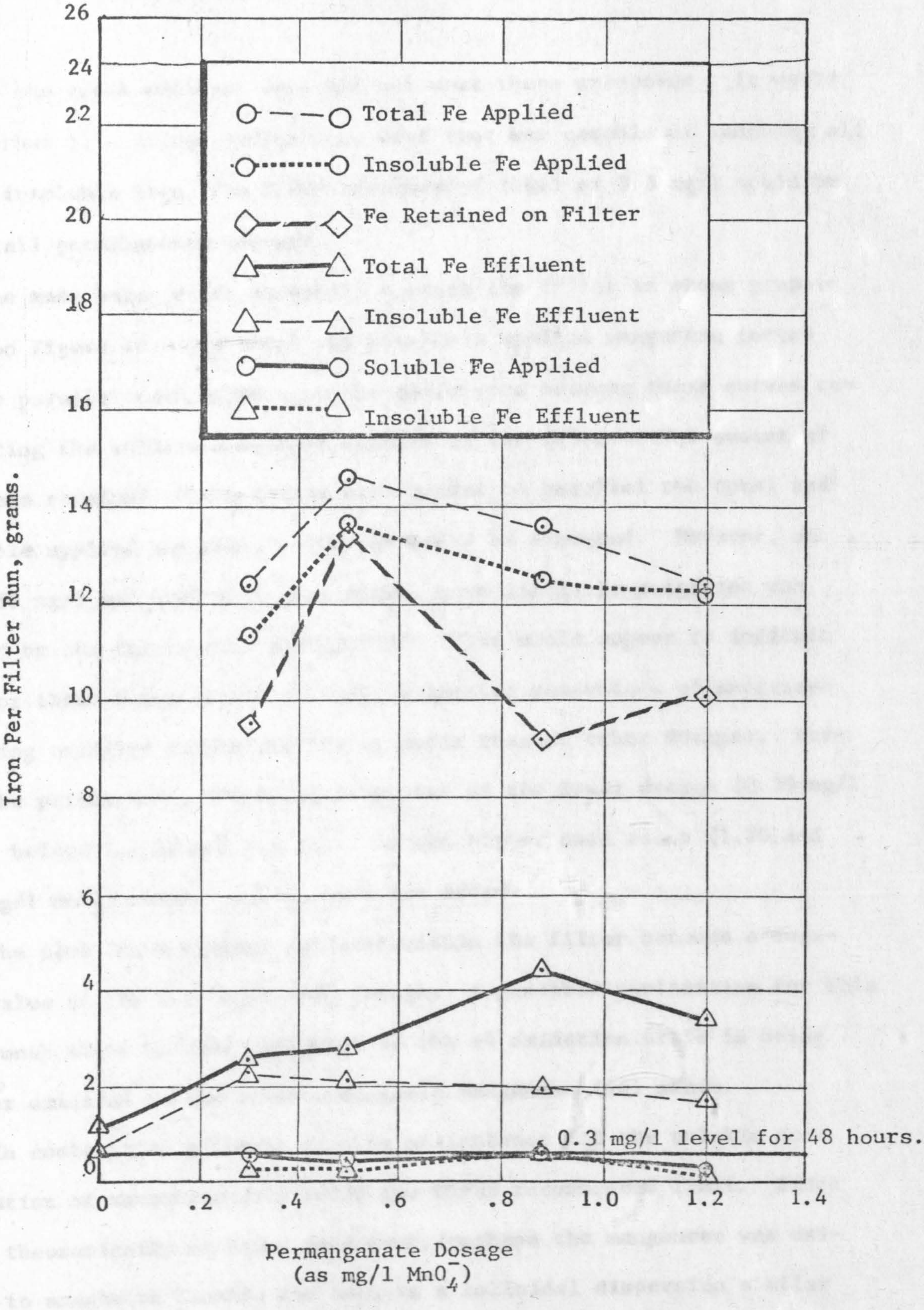

Figure 17. Mass Balance For Iron Through Pilot Filter Versus Permanganate Dosage.

filter, the total effluent iron did not meet these standards. It would appear that if a filter medium were used that was capable of removing all of the insoluble iron, the USPHS recommended limit of 0.3 mg/l could be met at all permanganate dosages.

The mass balance for manganese through the filter is shown graphically on Figure 18. The total and insoluble applied manganese curves tend to parallel each other with the difference between these curves representing the soluble manganese applied to the filter. The amount of manganese retained on the filter also tended to parallel the total and insoluble applied manganese curves as would be expected. However, at the 0.50 mg/l and 0.88 mg/l dose rates, more insoluble manganese was removed by the filter than was applied. This would appear to indicate that for these permanganate dosages, a greater percentage of manganese was being oxidized within the filter media than at other dosages. Perhaps the permanganate was being exhausted at the lower dosage (0.30 mg/l MnO_4^-) before the demand was met. At the higher dose rates (1.20 and 2.02 mg/l MnO_4^-) excess permanganate was added.

The plot for manganese oxidized within the filter becomes a negative value at the 2.02 mg/l MnO_4^- dosage. A possible explanation for this occurrence might be that manganese in the +4 oxidation state is being further oxidized to the soluble manganic manganese (+6) state.

In contrast to effluent iron in no instance did the soluble concentration of manganese drop below the USPHS recommended limit. Since $KMnO_4$ theoretically oxidizes manganese, perhaps the manganese was oxidized to manganese dioxide and held in a colloidal dispersion similar

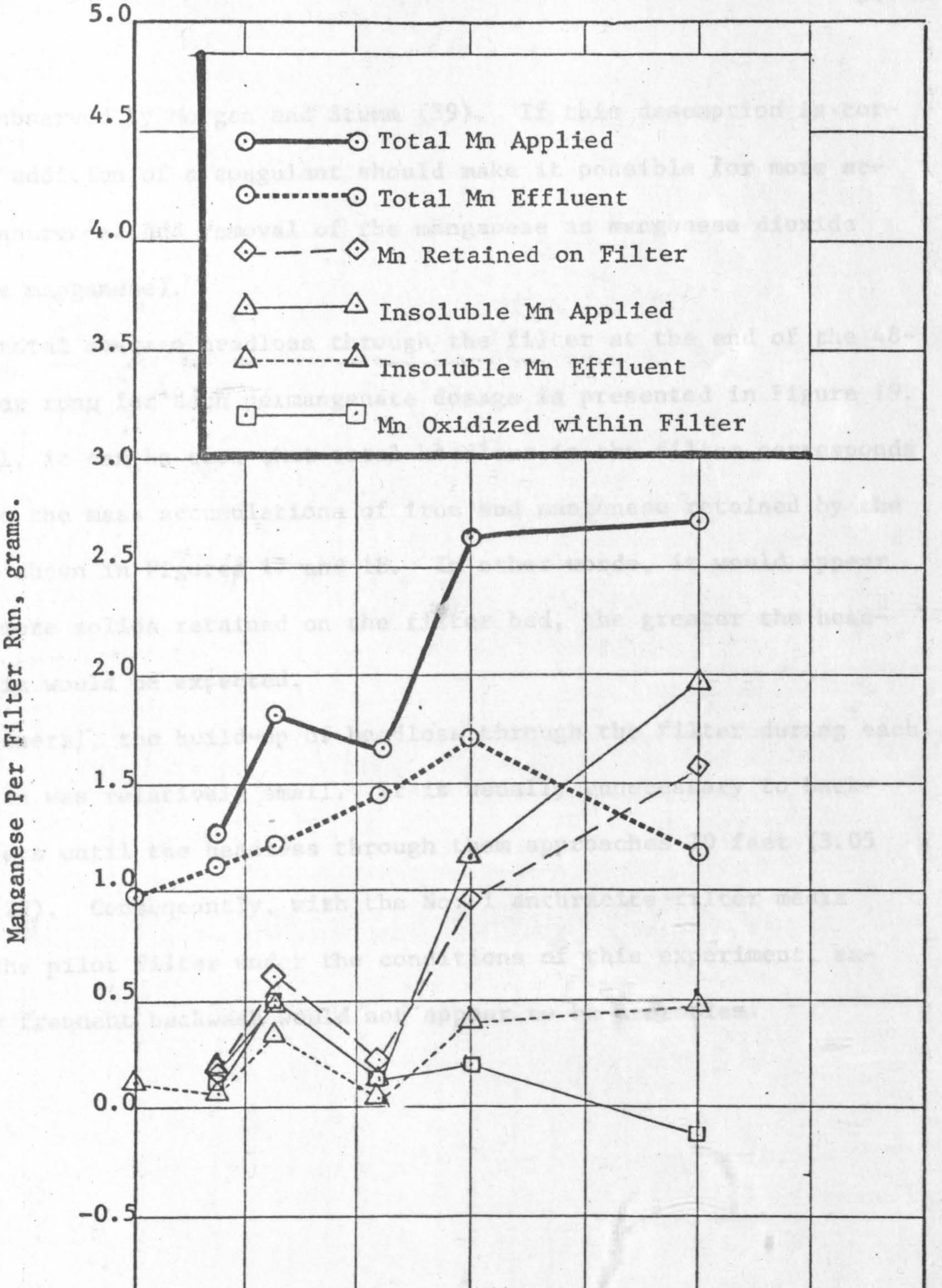

Figure 18. Mass Balance for Manganese Through Pilot Filter Versus Permanganate Dosage.

to those observed by Morgan and Stumm (39). If this assumption is correct, the addition of a coagulant should make it possible for more accurate measurement and removal of the manganese as manganese dioxide (insoluble manganese).

The total average headloss through the filter at the end of the 48-hour filter runs for each permanganate dosage is presented in Figure 19. In general, it can be seen that total headloss in the filter corresponds roughly to the mass accumulations of iron and manganese retained by the filter as shown in Figures 17 and 18. In other words, it would appear that the more solids retained on the filter bed, the greater the headloss. This would be expected.

In general, the build-up of headloss through the filter during each 48-hour run was relatively small. It is usually unnecessary to backwash filters until the headloss through them approaches 10 feet (3.05 meters) (27). Consequently, with the No. 1 anthracite filter media used in the pilot filter under the conditions of this experiment, excessively frequent backwash would not appear to be a problem.

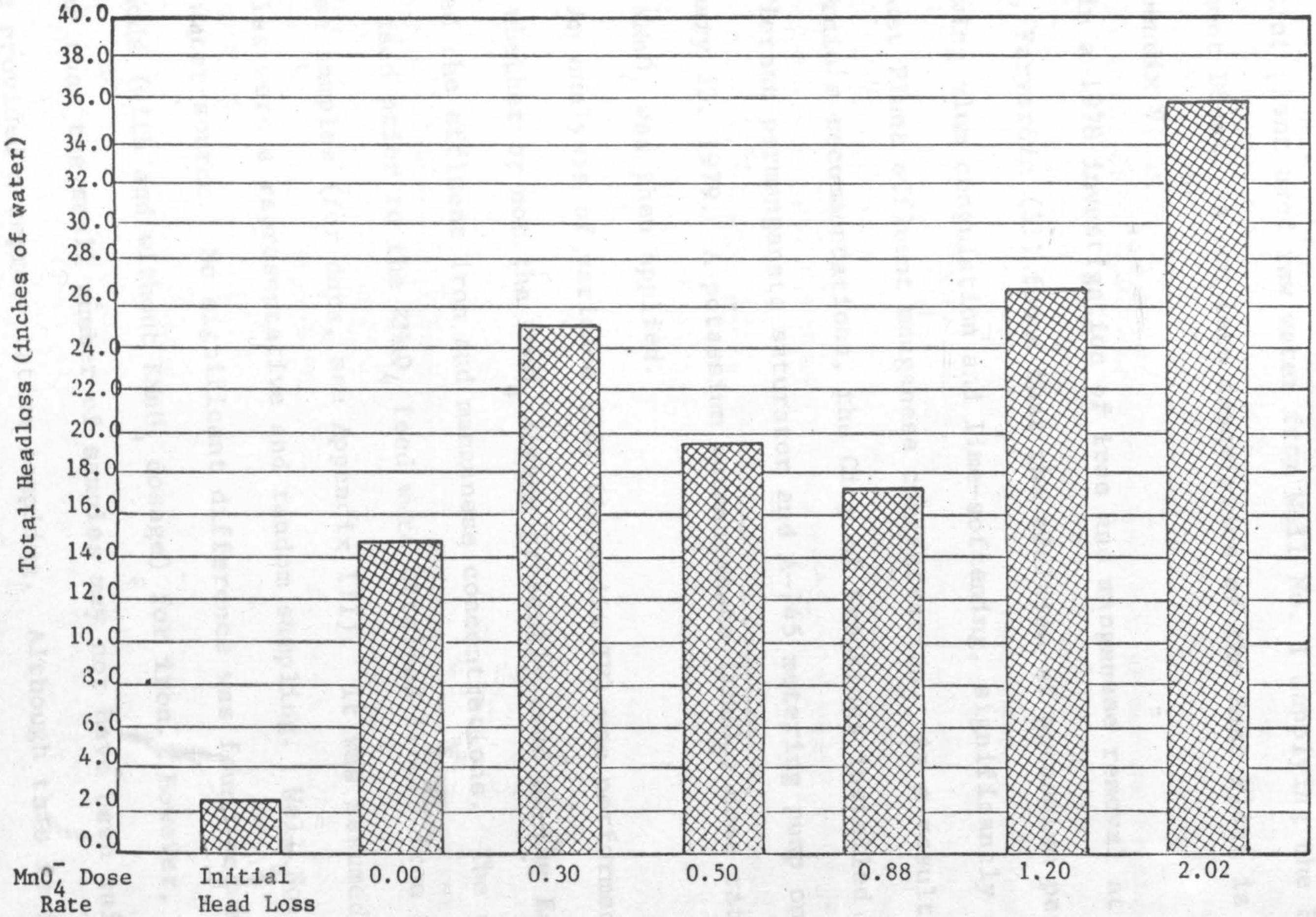

Figure 19. Comparison of Total Headloss at Varing Permanganate Dosage.

East Plant Iron and Manganese Removal Efficiencies

Brookings water supply is provided from two water treatment plants. The pilot plant used raw water from Well No. 1 supplying the East Water Treatment Plant. A complete description of the East Plant is presented in Appendix V.

In a 1978 investigation of iron and manganese removal at the East Plant, Farvardin (31) found that the addition of potassium permanganate following alum coagulation and lime-softening, significantly decreased the East Plant effluent manganese concentration. As a result of Farvardin's recommendations, the City of Brookings installed a Wallace and Tiernan permanganate saturator and A-745 metering pump on February 13, 1979. A potassium permanganate ($KMnO_4$) dose rate of 0.12 mg/l $KMnO_4$ was then applied.

An analysis of variance (38) (Appendix IV) was performed to determine whether or not the $KMnO_4$ dosage presently used at the East Plant affected the effluent iron and manganese concentrations. The data (Appendix III) used prior to the $KMnO_4$ feed were obtained from 3 iron and 10 manganese samples (for data, see Appendix III). It was assumed that these samples were a representative and random sampling. Well No. 1 was the raw-water source. No significant difference was found between treatment methods (with and without $KMnO_4$ dosage) for iron. However, it must be noted that the small number of samples may not have been sufficient to have provided a representative sampling. Although this is in agreement with the results obtained by Farvardin (31), past chemical analysis records for the East Plant (42) also show that the iron concentration has been below the recommended 0.3 mg/l limit and the permanganate treatment was intended as a means of reducing effluent manganese and not necessarily effluent iron. The analysis of variance did reveal a significant difference at the 0.010 level of significance existed between treatment methods. The mean difference being 0.07 mg/l Mn. The mean manganese concentration during permanganate treatment (based on 52 samples) was 0.02 ± 0.02 mg/l Mn. This is below the recommended 0.05 mg/l Mn limit.

Potassium permanganate, a proven disinfectant, (8) should also be expected to reduce the total chlorine demand of the treated water. This might be the case in the East Plant as well. The change in average chlorine dosage for the month of March for the years 1978 (before $KMnO_4$ feed) and 1979 (after $KMnO_4$ feed) is presented in Table 6. It can be seen that the chlorine dosage decreased from 1.89 mg/l to 1.53 mg/l, a 19 percent decrease.

Table 6. Chlorine Demand Comparison, Before and After $KMnO_4$ Feed. (42)

Month/Year	Water Produced at East Plant (gallons/month)	Chlorine Usage (pounds/month)	Chlorine Dose Rate (mg/l)
March 1978	34,455,000	542	1.89
March 1979	33,155,000	423	1.53

Note: The East Plant began to feed $KMnO_4$ on February 13, 1979.

Water Stability

The "water stability parameters" along with total hardness and dissolved oxygen, are presented in Figures 20 and 21. Each point represents the average of at least 4 determinations made during runs at each permanganate dose rate. A least-squares analysis of variance for the above parameters was performed by the Agricultural Experiment Station Statistician at South Dakota State University. The results of this statistical analysis (Appendix IV) reveal that there was no significant difference at the .01 level between dose rates and pilot effluent total and calcium hardness, alkalinity, pH, total dissolved solids, and dissolved oxygen. The temperature was significantly different at the .01 level. This was probably due to the variation in down time (up to 16 hours per day) experienced by the pilot plant. No significant difference existed for any of the parameters of the raw water and East Plant Effluent.

Table 7 includes the mean and standard deviation for the parameters used in calculation of the stability index. From Table 7 it can be seen that both the raw water and East Plant effluent were relatively stable waters, even though they are both categorized as "slightly corrosive". However, the approximation errors accompanied with analysis and the use of Lawrence-Caldwell Diagrams may have affected these results. The pilot plant effluent water was characterized as being oversaturated (SI = +.53). This scaling tendency was probably caused by the increases in pH brought about by aeration of the raw water in an attempt to reduce the permanganate demand. However, due to changes in temperature, which affect the solubility of dissolved gasses (ie. CO_2), it is difficult to draw definite conclusions regarding the influence of permanganate treatment on water stability.

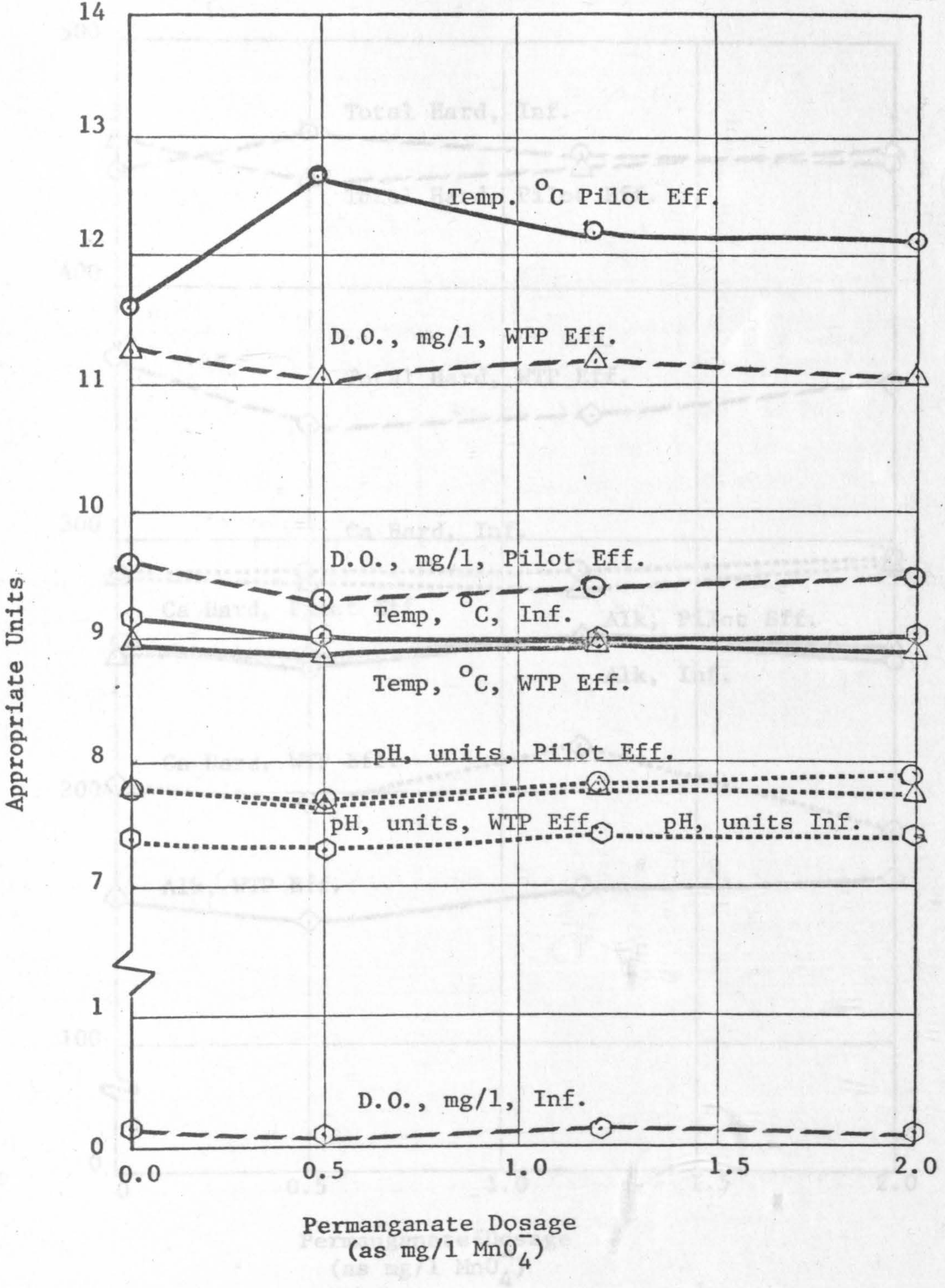

Figure 20. Temperature, pH, and Dissolved Oxygen of Pilot Unit and Water Treatment Plant Effluents.

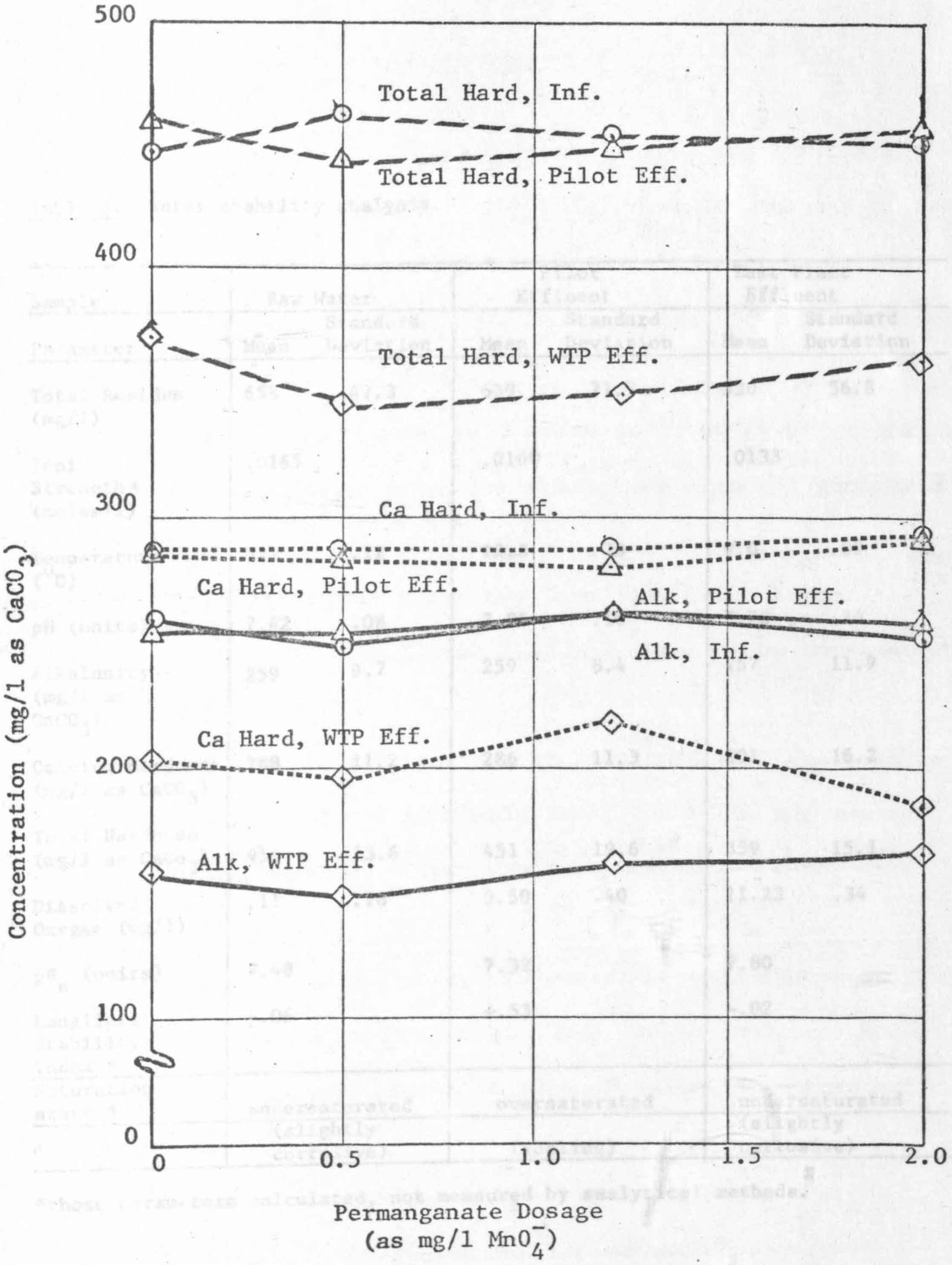

Figure 21. Total Hardness, Calcium Hardness, and Alkalinity of Pilot Unit and Water Treatment Plant Effluents.

Table 7. Water stability analysis.

Sample	Raw Water		Pilot Effluent		East Plant Effluent	
Parameter	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Total Residue (mg/l)	658	47.3	639	71.7	530	56.8
Ionic Strength* (moles/l)	.0165		.0160		.0133	
Temperature (°C)	9.1	.12	12.3	.70	9.0	.09
pH (units)	7.42	.08	7.85	.10	7.78	.14
Alkalanity (mg/l as $CaCO_3$)	259	9.7	259	8.4	157	11.9
Calcium Hardness (mg/l as $CaCO_3$)	288	11.2	286	11.3	201	16.2
Total Hardness (mg/l as $CaCo_3$)	454	13.6	451	19.6	359	15.1
Dissolved Oxygen (mg/l)	.11	.18	9.50	.40	11.23	.34
pH_s (units)	7.48		7.32		7.80	
Langliers Stability Index *	-.06		+.53		-.02	
Saturation state *	undersaturated		oversaturated		undersaturated	
	(slightly corrosive)		(scaling)		(slightly corrosive)	

*those parameters calculated, not measured by analytical methods.

CONCLUSIONS

Based upon an examination of the data collected, the following conclusions can be made regarding use of the pilot unit for removal of iron and manganese with aeration and potassium permanganate for oxidation.

1. Iron and manganese removals did not meet the USPHS recommended standards when feeding $KMnO_4$.
2. $KMnO_4$ seemed to act as an "anti-coagulant", which prevented the coagulation of ferric oxide particles, and actually increased the effluent iron concentration.
3. Aeration as an oxidant alone may have promoted a larger agglomeration of iron particles than did aeration in combination with $KMnO_4$.
4. It appears that if a filter medium were used that was capable of removing all of the insoluble iron, the USPHS recommended limit of 0.3 mg/1 total iron could be met at all $KMnO_4$ feed rates.
5. Either water characteristics prevented the oxidation-reduction reactions for manganese to take place, or the MnO_2 and Mn_2O_3 formed by these same reactions were of colloidal nature and did not agglomerate.
6. Total headloss through the filter varied with the $KMnO_4$ dosage applied to the filter and the amount of insoluble manganese retained within the filter.

7. The East Water Treatment Plant, Brookings, South Dakota presently operates using aeration, lime softening, alum, recarbonation, and $KMnO_4$ dosage. The filter effluent iron and manganese concentrations were significantly below the USPHS recommended standards during the period of March-June 1979.
8. A significant reduction in filter effluent manganese concentrations was noted at the East Plant as a result of feeding $KMnO_4$ at a dosage of 0.12 mg/l.
9. The addition of 0.12 mg/l $KMnO_4$ in the East Plant operations decreased the chlorine demand of the filter effluent by 19.0 percent.

RECOMMENDATIONS FOR FUTURE STUDY

The following recommendations are made for future studies involving the treatment of iron and manganese.

1. The use of a coagulant such as aluminum sulfate (Alum) or ferric sulfate may increase floc production by agglomeration so that the iron and manganese could be completely removed using No. 1 Anthracite.
2. Studies should be conducted to determine if a filter medium having a finer gradation than the No. 1 Anthracite used in these experiments might be successful in reducing effluent iron and manganese to meet USPHS recommended limits.
3. The use of manganese greensand should be tried in an attempt to improve iron and manganese removal efficiencies.
4. The use of $KMnO_4$ for disinfection augmented with chlorine to provide a residual should be evaluated as a possible means for reducing disinfection costs.
5. Theoretically, ozone will completely oxidize iron and manganese. The economics of such a removal procedure should be investigated.
6. The stability of the raw water seemed to be altered by aeration. The influence of aeration on water stability should be evaluated.

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APPENDIX I

Aerator Design

Design Criteria.

East Plant Design Filter Rate (42) = 2gpm/ft^2 filter media.

Pilot Filter diameter = 6-in

Pilot Filter area = $\pi \frac{(.5 \text{ ft})^2}{4}$ = .1963 ft^2

therefore, Pilot Flow Rate, Q = (2gpm/ft^2) (.1963 ft^2)

= .3927 gpm

= 1.4864 liters per minute (l/m)

Ten States Standards (32) states that the Loading Rate (L.R.) for the aerator should be:

$$1 \text{ gpm/ft}^2 \leq \text{LR} \leq 5\text{gpm/ft}^2$$

Given the minimum Aerator Loading Rate (LR) and Design Flow, (Q) of:

R = 1 gpm/ft^2

and Q = .4 gpm

the maximum aerator area is:

$$\text{Aerator Area} = \frac{.4\text{gpm}}{1 \text{ gpm/ft}^2}{}^2 = .4 \text{ ft}^2$$

or a maximum diameter of:

$$d_{\text{max}} = \sqrt{\frac{4\ (.4 \text{ ft}^2)}{\pi}} = .714 \text{ ft} = 8.56 \text{ in}$$

To determine the minimum diater of the aerator use:

LR = 5gpm/ft^2

Q = .4gpm

Using same procedure as before:

$$d_{\text{min}} = 3.8\text{-in}$$

Therefore:

$$3.8\text{-in} \leq d \leq 8.5\text{-in}$$

Diameter size used:

Dia = 6-in

Discharge the water over a series of 5 or more trays with tray separation at least 6-in and provide distribution of water uniformly over the top tray (32).

For 5 trays at 6-in apart the minimum height of the aerator is:

height = 4 x 6 = 24-in (2ft)

To be on the conservative side this design will use a height of:

Height = 4-ft

with 7 trays

Each tray installed at 7-in apart.

The top tray to be 3-in below the top of the aerator column and the bottom tray to be 3-in above the bottom of the column (Figure 3).

Ten States Standards does not provide any air velocity recommendations for countercurrent aerators. Therefore, the General Filter Co. Catalogue (41) was consulted. Typical air velocities varied:

$$61.1\text{ ft/min} \leq V_{air} \leq 88.9\text{ ft/min.}$$

the minimum air flow (Q_{air}) for a 6-in diameter aerator is:

$$Q_{air}(\text{min}) = 11.78\text{ cfm}$$

The smallest fan available in the Grainger Motor Book No. 349, W.W. Grainger, Inc., Sioux Falls, S.D. was a 55 cfm Dayton Box Fan manufactured by Daton Electric Manufacturing Co., Chicago, which was used to provide adequate air flow.

APPENDIX II

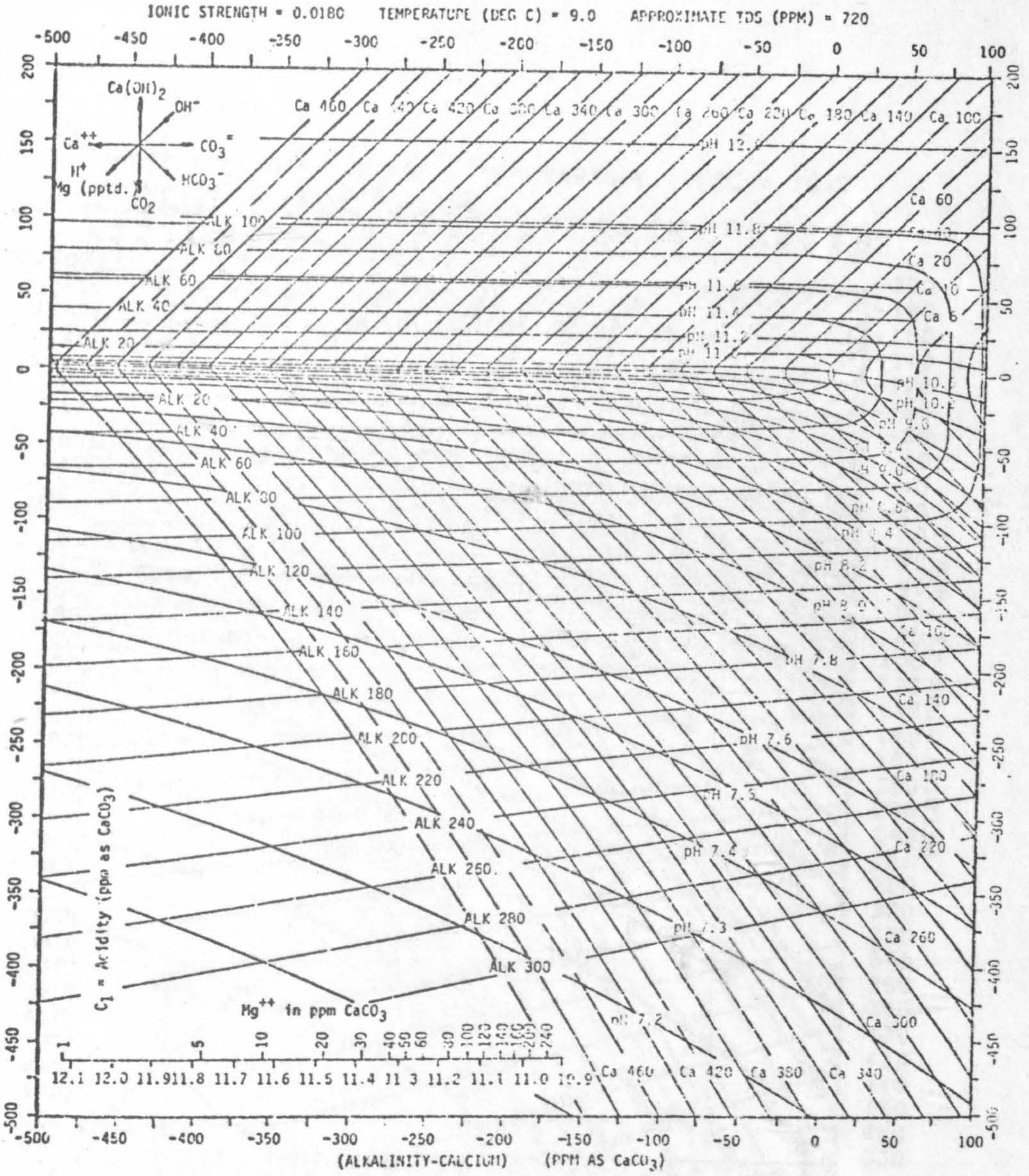

Figure 22A. Caldwell-Lawrence Diagram Used For Raw Water. (35)

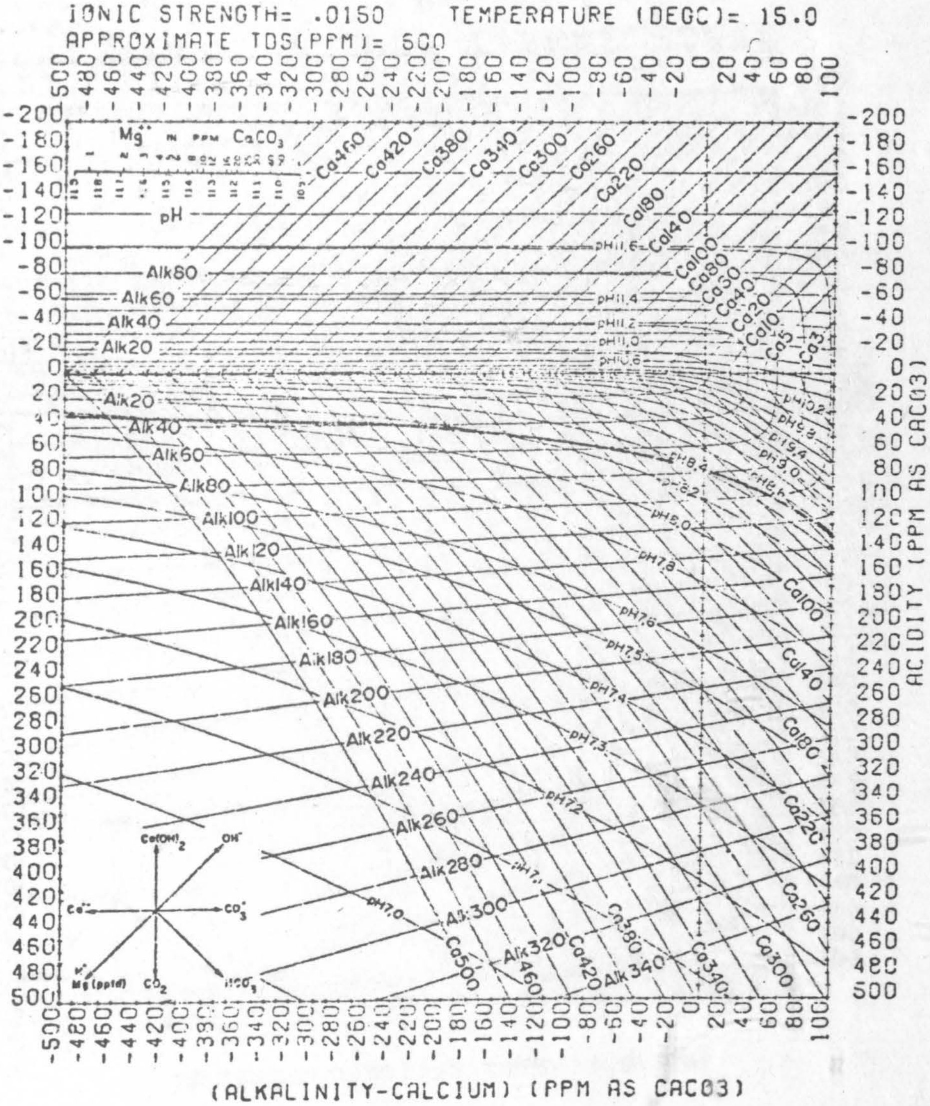

Figure 23A. Caldwell-Lawrence Diagram Used For The Pilot Plant Effluent. (37)

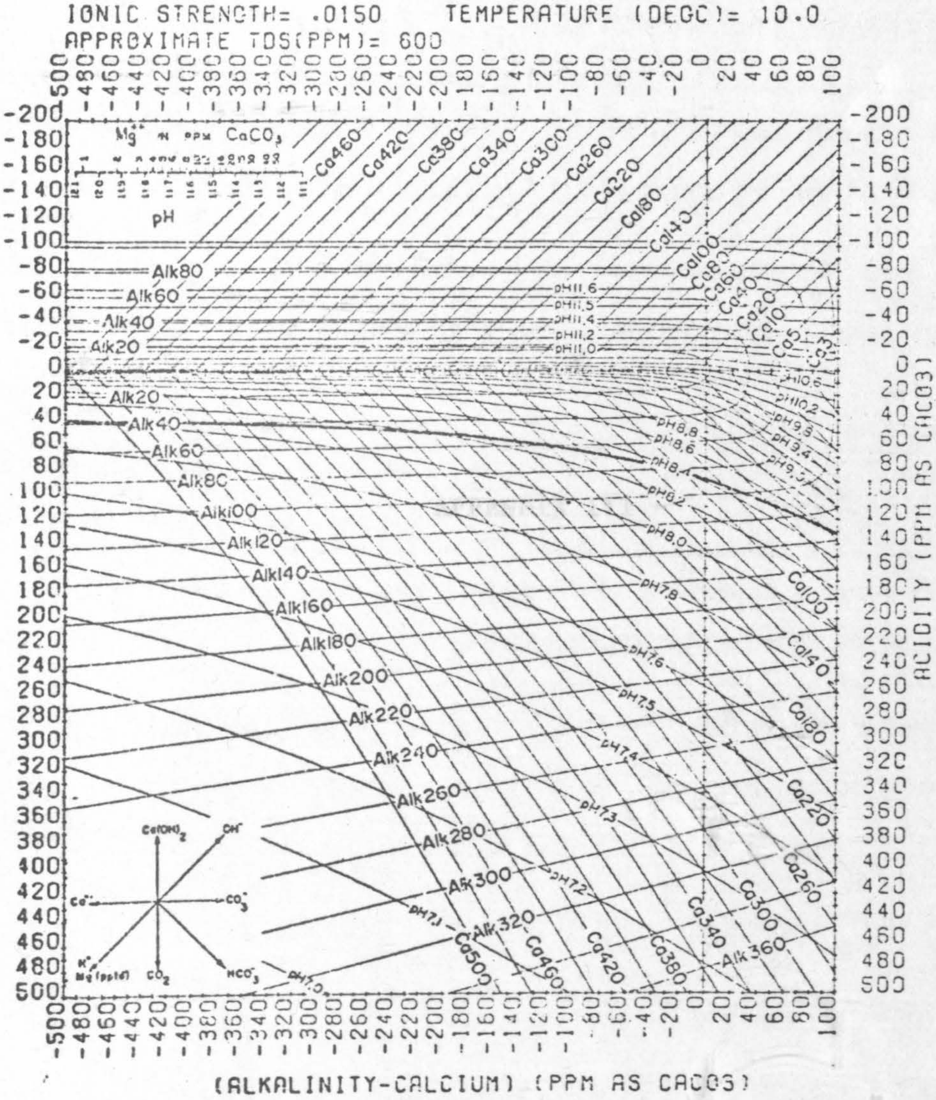

Figure 24A. Caldwell-Lawrence Diagram Used For The East Plant Effluent. (37)

APPENDIX III

<u>Table 8A</u>. Iron and Manganese Data Collected.

Date(1979)	Iron								Manganese								MnO_4^- Feed Rate (mg/1)	Time Since Backwash (hr:min)
	Raw Water		Reaction Basin Effluent		Pilot Filter Effluent		East Plant Effluent		Raw Water		Reaction Basin Effluent		Pilot Filter Effluent		East Plant Effluent			
	T*	S@	T	S	T	S	T	S	T	S	T	S	T	S	T	S		
Jan. 5	3.8	3.6			.20	.10		.10	.65	.55			.42	.31	.14	.14	0	7:26
Jan. 6	3.5	3.3			.45	.10	.14	.18	.60	.60			.60	.50	.17	.14	0	17:01
Jan. 7	3.2	3.4			.20	.10	.20	.12	.60	.60			.50	.50	.17	.14	0	29:36
Jan. 8	3.5	3.4			.18	.12	.26	.18	.55	.60			.50	.50	.17	.14	0	43:12
Jan. 19									.56	.43			.49	.44	.05	.04	0	14:56
Jan. 20									.55	.45			.46	.39	.05	.04	0	32:27
Jan. 21									.54	.53			.51	.41	.05	.00	0	50:00
Jan. 25									.45	.42			.40	.36	.04	.03	0	4:10
Jan. 26									.40	.41			.34	.40	.04	.03	0	23:03
Jan. 27									.44	.39			.39		.05		0	53:34
Feb. 13									.60	.51	1.4	.14	.30		.00		1.91	11:20
Feb. 14									.50	.41	1.0	.17	.60		.02		2.02	28:36
Feb. 14									.60	.44	1.3	.21	.40		.04		2.04	33:43
Feb. 15									.50	.43	1.3	.14	.80		.01		1.97	45:50
Feb. 21									.59		1.4	.63	.37	.38	.07	.04	1.97	11:48
Feb. 22									.41	.41	1.2	.20	.46	.23	.05	.04	2.05	24:48
Feb. 22									.41	.41	1.1	.47	.63	.45	.06	.04	2.19	37:47
Feb. 23									.41	.41	1.4	.79	.76	.52	.05	.05	1.96	51:26
Mar. 1	3.0	2.8		.09	.26	.09	.07	.07	.80	.80	1.3	.88	.93	.98	.03	.02	1.22	11:18
Mar. 2	2.7	2.6	3.7	.00	.70	.14	.12	.00	.75	.80	1.5	.77	.94	.85	.00	.00	1.32	25:50
Mar. 2	2.9	3.4	2.1		.02	.02	.02	.04	.75	.75	1.4	.70	.83	.60	.00	.00	1.41	30:13
Mar. 4	3.4	3.6	2.9	.33	.18	.02	.01	.00	.75	.75	1.3	.44	.67	.56	.01	.00	1.14	56:43
Mar. 6	3.4	3.5	2.4	.10	.84	.04	.05	.06	.80	.60	1.3	.67	.93	.65	.00	.00	1.12	18:18
Mar. 7	3.0	2.3	2.6	.09	.31	.00	.15	.21			.80	.88		.75	.00	.01	1.19	28:39
Mar. 8	3.9	3.4	2.1	.21	1.18	.09	.21	.14	.60	.60	1.3	.55	.72	.63	.01	.00	1.25	40:21
Mar. 8	2.4	2.3	3.6	.21	1.05	.41	.43	.04	.80	.65	1.2	.55	.84	.87	.03	.02	1.16	50:49
Mar. 9	3.5	3.5	3.2	.09	.20	.00	.00	.18	.55	.60	1.1	.84	.84	.81	.00	.02	1.14	11:26
Mar. 10	5.1	4.9	4.1	.04	.36	.26	.00	.06	.75	.75	1.3	.91	.63	.42	.00	.00	1.19	21:01
Mar. 11	4.6	4.6	2.0	.07	.33	.00	.00	.03	.80	.70	1.2	.94	.61		.00	.03	1.16	34:01
Mar. 12	4.4	4.1	3.0		4.1	.12	.00	.00	.70	.60	1.3		1.1	.74	.00	.00	1.09	49:19
Mar. 15	4.3	4.5	3.4	.03	.35	.05	.15	.15	.90	.90	1.2	.88	.90		.00	.02	.58	14:14
Mar. 15	4.8	4.1	3.5	.37	.56	.11	.00	.01	.80	.90	1.2	.85	.59	.66	.03	.03	.46	20:04
Mar. 16	4.5	4.5	3.7	.06	.32	.00	.07	.09	.90	.80	1.2	.83	.80	.78	.02	.01	.43	32:03

Date(1979)	Iron								Manganese								MnO_4^- Feed Rate (mg/l)	Time Since Backwash (hr:min)
	Raw Water		Reaction Basin Effluent		Pilot Filter Effluent		East Plant Effluent		Raw Water		Reaction Basin Effluent		Pilot Filter Effluent		East Plant Effluent			
	T	S	T	S	T	S	T	S	T	S	T	S	T	S	T	S		
Mar. 21	4.3	4.6	3.4	.25	.63	.20	.12	.10	.50	.50	.70	.66	.33	.35	.01	.01	.49	57:33
Mar. 21	5.5	5.4	4.8	.22	.36	.17	.15	.16	.50	.50	.80	.75	.58	.53	.01	.00	.52	9:58
Mar. 22	4.8	4.6	3.8	.23	.75	.30	.20	.10	.50	.50	.70	.62	.45	.43	.01	.01	.53	22:17
Mar. 23	4.2	3.7	2.9	.16		.02	.18	.18	.60	.50	.62	.59	.58	.54	.02	.01	.54	40:37
Mar. 23	4.7	3.9	3.4	.23	.69	.15	.72	.11	.50	.60	.70	.68	.60	.46	.07	.02	.56	50:40
Mar. 28	4.3	4.1	3.3	.11	.19	.28	.16	.23	.60	.70	.80	.63	.41	.45	.01	.02	.45	15:05
Mar. 29	4.5	3.9	1.7	.38	.07	.11	.08	.12	.60	.60	.70	.40	.61				.506	36:33
Mar. 30	4.8	4.9	3.1	.18	.46	.18	.14	.21	.60	.70	.70		.40	.30	.00	.02	.45	52:11
May 16	4.1	3.7	3.1	.40	.74	.52	.15	.13	.55	.40	.40	.55	.44	.44	.02	.02	.22	11:55
May 17	3.9	3.8	2.9	.20	.63	.13	.20	.08	.40	.55	.50	.61	.61	.53	.00	.02	.25	23:55
May 18	3.4	3.8	2.8	.29		.11	.13	.15	.40	.40	.55	.55	.61	.59	.02	.02		
May 19	4.0	3.8	2.8	.33	.83	.03	.00	.11	.40	.40	.60		.57	.57	.03	.02	.28	57:12
May 20	4.5	4.0	3.4	.34	.23	.21	.19	.05	.80	.60	.60	.54	.53	.57	.03	.00	.29	13:25
May 22	4.5	4.0	2.9	.32	.33	.17	.04	.05	.60	.60	.80	.50	.51	.42	.02	.02	.31	49:29
May 23	3.8	3.9	2.0	.04	.05	.01	.03	.03	.80	.70	.80	.58	.51	.51	.03	.03	.32	16:00
May 24	3.9	3.7	2.7	.05	.52	.05	.15	.18	.38	.28	.61	.57	.41	.40	.02	.02	.22	24:14
May 25	3.7	3.7	3.1	.06	.73	.03	.17	.08	.51	.54	.59	.56	.56	.52	.01	.01	.28	40:18
May 26	3.7	3.7	2.9	.35	1.9	.13	.06	.07	.52	.50	.46	.53	.46	.37	.09	.07	.25	52:15
May 28	3.9	3.6	3.1	.06	.87	.27	.30	.22	.60	.50	1.1	.71	.64	.70	.01	.01	.86	14:22
May 29	4.1	3.5	2.9	.06	.63	.07	.11	.11	.80	.40	.40	.60	.69	.55	.00	.00	.75	23:42
May 29	3.9	3.6	3.7	.49	1.0	.10	.25	.16	.54	.58	.79	.79	.70	.71	.03	.02	.89	35:20
May 30	3.6	3.4	3.9	.14	1.8	.09	.03	.09	.48	.57	.84	.77	.71	.71	.03	.01	.86	48:06
May 30	4.1	3.7	3.0	.32	.61	.25	.24	.35	.48	.48	.79	.75	.60	.59	.02	.05	.93	13:23
May 31	4.0	3.7	2.8	.17	.79	.16	.22	.22	.48	.48	.55	.66	.78	.76	.03	.01	.98	22:51
May 31	3.8	4.2	3.2	.30	.80	.26	.17	.19	.52	.62	.91	.78	.72	.77	.02	.01	.80	33:46
June 1	4.1	5.3	3.3	.16	1.4	.47	.28	.20	.47	.48	.74	.66	.48	.53	.02	.02	.85	48:03
June 2	5.0	4.6	3.0	.46	.78	.32	.36	.28	.51	.49	.80	.61	.72	.69	.00	.00	.84	9:58
June 2	4.6	4.5	2.9	.38	1.1	.36	.32	.29	.42	.45	.77	.68	.56	.48	.00	.00	.89	22:43
June 3	4.0	4.4	2.8	.46	1.0	.27	.26	.27	.47	.30	.78	.81	.66	.63	.01	.01	.91	34:58
June 3	4.2	4.4	3.2	.10	1.4	.15	.30	.24	.55	.53	.81	.71	.79	.73	.01	.01	.96	48:19

* T - refers to total metal concentration (mg/l)
@ S - refers to soluble metal concentration (mg/l)

Table 9A. Raw Water Stability Parameter Data

Parameter / Date	Total Hardness mg/l as $CaCO_3$	Calcium Hardness mg/l as $CaCO_3$	Alkalinity mg/l as $CaCO_3$	pH units	Temperature ^{o}C	Total Residue mg/l	Dissolved Oxygen mg/l
Jan 6	431	282	262	7.22	9.4	634	0.10
Jan 9	480	272	266	7.50	9.0	646	0.00
Jan 20	442	285	263	7.42	9.2	627	0.16
Jan 21	440	288	261	7.48	9.0	615	0.42
Jan 27	442	303	254	7.48	9.2	629	0.00
Jan 28	454	304	262	7.46	9.0	645	0.14
Feb 14	444	284	270	7.38	9.0	671	0.00
Feb 15	445	286	259	7.48	9.0	642	0.02
Feb 20	461	308	253	7.52	9.2	641	0.00
Feb 27	455	292	259	7.36	9.2	740	0.30
Mar 1	461	290	258	7.30	9.0	594	0.00
Mar 2	453	276	266	7.38	9.0	552	0.00
Mar 6	458	288	250	7.50	9.0	759	0.06
Mar 8	450	292	259	7.56	9.0	639	0.00
Mar 9	459	283	272	7.52	9.0	653	0.00
Mar 11	448	270	287	7.38	9.0	660	0.72
Mar 15	448	281	258	7.38	9.0	663	0.04
Mar 21	452	277	259	7.42	9.2	711	0.00
Mar 22	453	283	252	7.40	9.2	675	0.34
Mar 23	455	282	249	7.40	9.2	667	0.06
Mar 29	476	310	242	7.36	9.0	690	0.00
Mar 30	490	301	245	7.36	9.0	727	0.10
Mean	454	288	259	7.42	9.08	658	0.11
Standard Deviation	11.8	6.2	5.4	0.08	0.11	37.6	0.19

Table 10A. **Pilot Effluent Stability Parameter Data**

Parameter Date	Total Hardness mg/l as $CaCO_3$	Calcium Hardness mg/l as $CaCO_3$	Alkalinity mg/l as $CaCO_3$	pH units	Temperature ^{o}C	Total Residue mg/l	Dissolved Oxygen mg/l	Mean Dose Rate mg/l MnO_4^-
Jan 6	430	282	264	7.70	11.6	620	9.52	0.00
Jan 9	440	275	256	7.82	10.6	598	9.58	0.00
Jan 20	454	284	258	7.98	11.4	643	9.38	0.00
Jan 21	454	291	255	7.78	11.2	656	9.46	0.00
Jan 27	515	297	252	7.92	12.8	674	9.60	0.00
Jan 28	468	304	258	7.84	12.4	670	10.48	0.00
Feb 14	465	282	254	7.88	12.6	658	9.96	2.02
Feb 15	443	302	263	7.88	12.2	650	9.12	2.02
Feb 20	470	311	251	8.04	12.0	737	9.70	2.02
Feb 27	453	279	250	8.00	12.2	684	9.36	2.02
Mar 1	458	285	257	7.90	12.0	683	9.00	1.20
Mar 2	471	320	264	7.72	12.2	542	9.24	1.20
Mar 6	439	288	267	7.98	13.0	671	9.82	1.20
Mar 8	446	290	262	7.96	12.0	720	9.50	1.20
Mar 9	442	274	287	7.86	12.2	541	9.96	1.20
Mar 11	443	287	255	7.80	13.0	730	9.08	1.20
Mar 15	448	288	257	7.78	12.6	646	9.48	0.50
Mar 21	441	282	265	7.86	13.4	505	8.88	0.50
Mar 22	446	286	254	7.88	12.0	500	9.88	0.50
Mar 23	447	286	246	7.74	11.8	542	9.92	0.50
Mar 29	435	291	252	7.70	13.4	699	8.98	0.50
Mar 30	444	284	264	7.72	13.0	704	9.06	0.50
Mean	452	289	258	7.85	12.3	639	9.05	
Standard Deviation	12.5	11.8	8.4	.08	0.42	60.9	0.364	

Table 11A. East Plant Effluent Stability Parameter Data

Parameter Date	Total Hardness mg/l as $CaCO_3$	Calcium Hardness mg/l as $CaCO_3$	Alkalinity mg/l as $CaCO_3$	pH units	Temperature °C	Total Residue mg/l	Dissolved Oxygen mg/l
Jan 6	358	199	168	7.82	9.0	523	11.20
Jan 9	350	195	139	7.82	9.0	510	11.40
Jan 20	373	206	166	7.90	9.0	515	11.14
Jan 21	371	200	159	7.70	9.0	521	11.26
Jan 27	400	208	158	7.76	9.0	529	11.48
Jan 28	387	225	165	8.06	9.0	518	11.78
Feb 14	357	248	170	7.90	9.0	577	10.74
Feb 15	358	201	164	7.74	8.8	521	11.28
Feb 20	381	219	164	7.86	9.0	538	11.22
Feb 27	360	212	177	7.70	9.0	601	11.24
Mar 1	357	222	127	7.38	9.0		11.28
Mar 2	359	196	162	7.78	9.2	470	11.16
Mar 6	347	197	155	7.78	9.0	434	10.78
Mar 8	358	196	166	7.86	8.8	539	11.48
Mar 9	345	192	160	7.92	9.0	432	11.26
Mar 11	345	190	164	7.78	9.0	665	11.58
Mar 15	351	194	158	7.72	8.8	538	11.40
Mar 21	351	186	143	7.86	9.0	549	11.32
Mar 22	343	191	151	7.86	9.0	453	10.14
Mar 23	306	184	140	7.54	8.8	488	11.08
Mar 29	344	179	147	7.58	9.0	584	11.12
Mar 30	343	184	156	7.80	9.0	618	11.64
Mean	358	201	157	7.78	9.0	545	11.23
Standard Deviation	6.7	12.5	11.5	0.156	.095	103.2	0.316

APPENDIX IV

Table 12A. Analysis of Variance, Reaction Basin Effluent Iron and Manganese

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
		Total Iron		
Total	43	15.0111		
Between Dosage	3	1.8784	.6261	1.907
Within Dosage	40	13.1326	.3283	
		Soluble Iron		
Total	41	.7467		
Between Dosage	3	.0862	.0288	1.6541
Within Dosage	38	.6605	.0174	
		Difference Between Total and Soluble Manganese		
Total	50	6.7518		
Between Dosage	4	4.8238	1.2060	28.7731**
Within Dosage	46	1.9280	.0419	
		Soluble Manganese		
Total	49	1.9393		
Between Dosage	4	.9564	.2391	10.9679**
Within Dosage	45	.9829	.0218	

* Significant differance exists at the 0.05 level of significance.
** Significant differance exists at the 0.005 level of significance.

Table 13A. Analysis of Variance, Pilot Filter Effluent Iron and Manganese

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
		Total Iron		
Total	47	21.5679		
Between Dosages	4	3.3735	.8434	1.993
Within Dosages	43	18.1944	.4231	
		Soluble Iron		
Total	48	.7470		
Between Dosages	4	.1203	.0301	2.112
Within Dosages	44	.6267	.0142	
		Total Manganese		
Total	52	4.95		
Between Dosages	4	3.50	.88	29.13**
Within Dosages	48	1.45	.03	
		Soluble Manganese		
Total	49	1.9393		
Between Dosages	4	.9564	.2391	10.9679**
Within Dosages	45	.9829	.0218	

* Significant difference exists at the 0.05 level of significance.
** Significant difference exists at the 0.005 level of significance.

Table 14A. Analysis of Variance, Affect due to $KMnO_4$ addition for East Plant Effluent.

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
		Total Iron		
Total	47	.8489		
Between Dosages	1	.0056	.0056	.3055
Within Dosages	46	.8433	.0183	
		Total Manganese		
Total	61	.1001		
Between Dosages	1	.0454	.0454	49.8**
Within Dosages	60	.0547	.0009	

* Significant difference exists at the 0.05 level of significance.

** Significant difference exists at the 0.005 level of significance.

Table 15A. Analysis of Variance Mean Squares for Raw Water Stability Parameters.[1]

Source	Degrees of Freedom	Total Hardness	Calcium Hardness	Alkalinity	pH	Temperature	Total Residue	Dissolved Oxygen
TOTAL	21							
DOSE	3	201.3704	135.6204	227.1111	.003551	.019259	4207.7037	.002884
RUN[2]	2	183.6806**	449.1801	90.6250	.010868	.013889	2662.5139	.051118
DOSE X RUN	5	267.3778**	211.7944	162.4000**	.006126	.013111	2820.1944	.037019
WITHIN SAMPLE	11	138.6818	38.5909	28.6364	.006782	.012727	1415.2727	.036345

[1] The table was copied from a computer analysis printout.

[2] Assuming runs to be repititions, therefore random effects.

* Those values in which the observed significance level was less than 0.05.

** Those values in which the observed significance level was less than 0.01.

Table 16A. Analysis of Variance Mean Squares for Pilot Effluent Stability Parameters.[1]

Source	Degrees of Freedom	Total Hardness	Calcium Hardness	Alkalinity	pH	Temperature	Total Residue	Dissolved Oxygen
TOTAL	21							
DOSE	3	381.4514	49.8218	116.9884	.020018	1.2015	8226.0995	.1057
RUN	2	205.2813	4.0451	52.1285	.023951*	1.4139**	9184.2535	.1629
DOSE X RUN	5	729.8708*	197.7819	43.9486	.006926	0.4311**	6165.6819	.2530
WITHIN SAMPLE	11	156.0000	138.8182	70.9545	.005845	0.1782	3707.2273	.1322

[1] The table was copied from a computer analysis printout.

* Those values which the observed significance level was less than 0.05.

** Those values which the observed significance level was less than 0.01.

Table 17A. Analysis of Variance Mean Squares for East Plant Effluent Stability Parameters.[1]

Source	Degrees of Freedom	Total Hardness	Calcium Hardness	Alkalinity	pH	Temperature	Total Residue	Dissolved Oxygen
TOTAL	21							
DOSE	3	796.8056	900.0648*	356.3403*	.01758	.00620	3057.1759	0.07287
RUN	2	112.5000	41.8889	129.5313	.00946	.00347	7956.8472	0.19906
DOSE X RUN	5	348.3333**	162.5778	53.6375	.01923	.01128	7264.1111	0.14230
WITHIN SAMPLE	11	44.2727	155.3636	133.3182	.02444	.00909	10656.7273	0.10016

[1] The table was copied from a computer analysis printout.

* Those values in which the observed significance level was less than 0.05.

** Those values in which the observed singificance level was less than 0.01.

APPENDIX V

Description of the East Water Treatment Plant (31)

The Brookings East Water Treatment Plant, which has a design capacity of 10.5 m^3/min. (4 mgd), obtains its water supply from three wells approximately one mile east of the plant. The aquifer covers approximately 52 square kilometers (20 sq mi), and has a drainage area of about 337 sq km (130 sq mi). This provides an average annual recharge of 34 million cubic meters (9 billion gallons). The geohydraulic characteristics of the wells are presented in Table 18A. Table 19A contains a fairly complete characterization of the wells and finished waters.

A flow diagram of the plant is presented in Figure 25A. The water is pumped from the wells through a 50-cm (20 in) transmission line. The water enters the aerator through two 30-cm (12 in) inlet pipes. The aerator is of the induced draft type with capacity of 10.5 m^3/min (2800 gpm). In addition to aeration, the aerator strips such gasses as CO_2 and H_2S from the water.

Following aeration, the water enters the solids contact upflow basin. This unit has a water depth of 5.82 m (19 ft, 1 in), a diameter of 18.0 m (59 ft) and a detention time of 145 minutes at design flow. Lime for pH adjustment and aluminum sulfate (alum) for coagulation, are added to the mixing zone of this unit. The floc particles, which settle to the bottom of the basin, are removed automatically. The clarified water is withdrawn from the surface of the basin through launder troughs and flows to the recarbonation basin.

The recarbonation basin has a detention time of 20 minutes at design flow. Since the present demand is approximately one third of the design flow (the discharge from one well), the basin has been partitioned to maintain the 20 minute detention time. The resultant dimensions of the basin are: 6.1 m (20 ft) length, 5.2 m (17 ft) width, and 2.7 m (9 ft) water depth. The purpose of this unit is to combine CO_2 with the dissolved calcium carbonate and convert it to bicarbonate form to prevent the build-up of carbonate on the grains of the filter medium, and also to stabilize the water.

Table 18A. Geohydraulic Characteristics of Supply Wells, East Plant.[1]

Parameter	Well 1	Well 2	Well 3
Depth	19.8 m (65 ft)	19.8 m (65 ft)	19.8 m (65 ft)
Diameter (casing)	0.60 m (24 in)	0.60 m (24 in)	0.60 m (24 in)
Discharge (measured 1-22-78	231 m^3/h (1017 gpm)	229.6 m^3/h (1011 gpm)	266.4 m^3/h (1173 gpm)
Drawdown	5.4 m/24 hrs (17.75 ft)/ 24 hrs	3.92 m/5.5 hrs (12.92 ft)/ 5/5 hrs	3.55 m/8.5 hrs (11.67 ft)/ 8.5 hrs

Approximate well log:

Depth	Log
0 - 0.9 m (0 - 3 ft)	Topsoil
0.9 - 15.2 m (3 - 50 ft)	Fine Sand
15.2 - 15.8 m (50 - 52 ft)	Blue Clay
15.8 - 19.8 (52 - 65 ft)	Gravel and Sand

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[1] Data in this table obtained from Water Department records, City of Brookings, SD.

Table 19A. Typical Water Analyses, East Plant, in mg/l.[1]

Parameters	Well 1 mg/1	Well 2 mg/1	Well 3 mg/1	Finished Water mg/1
pH	7.29	7.34	7.4	7.92
Alkalinity (CaC_3)	253.0	253.3	246.5	200.0
Bicarbonate HCo_3(u $CaCo_3$)	308.5	309	300.5	244.0
Total Hardness	408.0	455.0	487.0	372.7
Calcium Hardness (Ca)	96.65	116.7	122.5	90.1
Magnesium Hardness (Mg)	32.74	43.9	43.95	35.8
Conductivity moh/cm	685.0	867.0	890	731.3
Total solids	620.0	712.0	748	548.0
Dissolved oxygen	0.0	0.0	0.0	11.1
Iron Fe	2.88	3.72	4.3	0.07
Manganese (Mn)	0.38	0.64	0.68	0.05
Chloride (Cl)	4.75	7.6	11.3	7.17
Sulfate (SO_4)	132.40	249.0	283	195.0
Nitrate (as N)	0.10	0.1	0.1	0.1
Fluoride (F)	0.26	0.25	0.25	0.91
Sodium (Na)	11.0	18.8	17.5	16.2
Potassium (K)	2.43	2.92	3.05	2.78
Chlorine Residual	-	-	-	0.80
Measurements	2	3	2	3

[1] Except pH

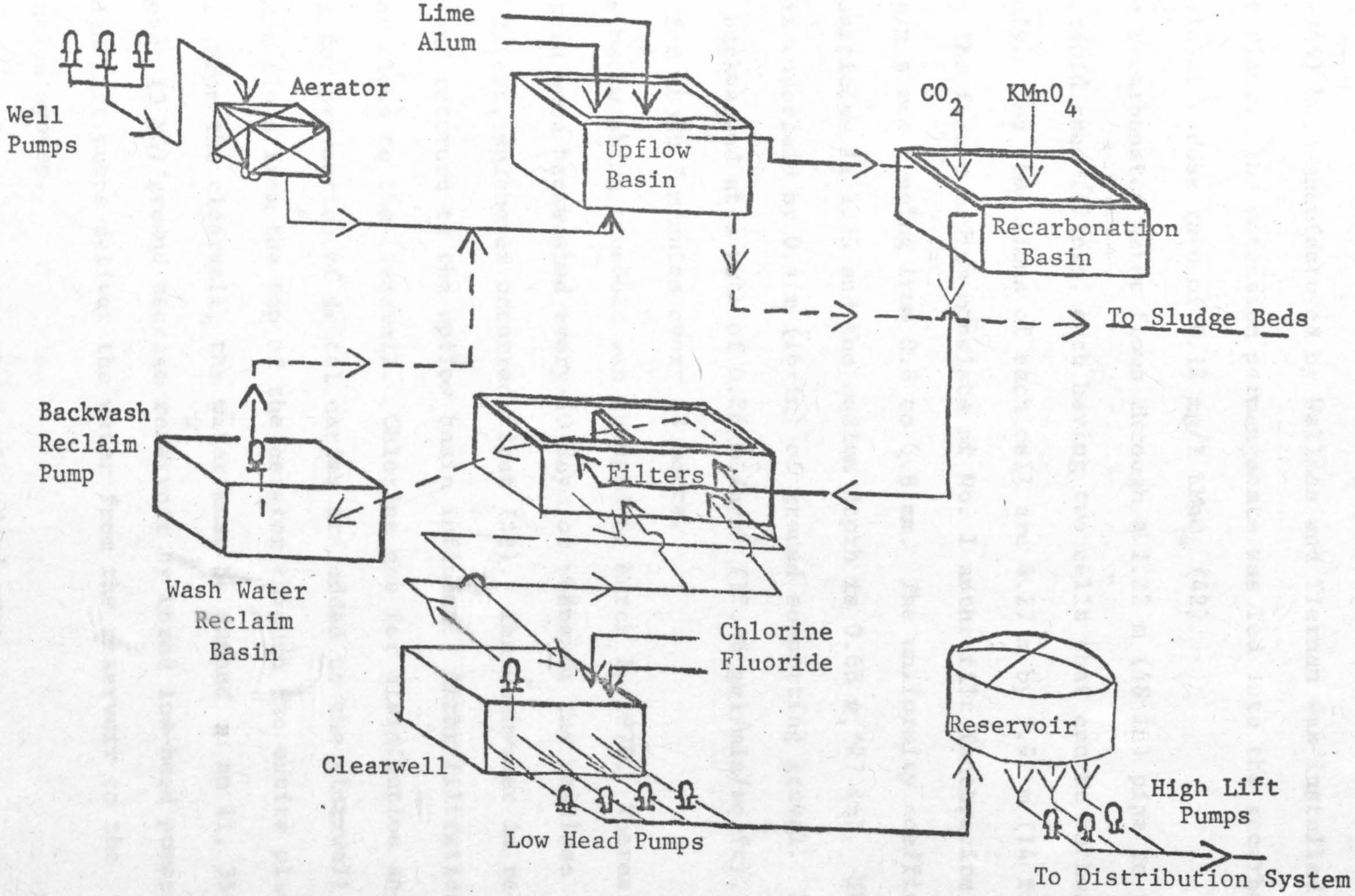

Figure 26A. Flow Diagram and Units of the East Treatment Plant, Brookings, South Dakota.

February 12, 1979 a permanganate saturator equipped with a metering pump (A-745) both manufactured by Wallace and Tiernan was installed at the East Plant. The potassium permanganate was fed into the recarbonation basin at a dose rate of 0.12 mg/l $KMnO_4$ (42).

The recarbonated water flows through a 1.22 m (48-in) pipe to two gravity rapid sand filters, each having two cells that can be backwashed separately. The dimensions of each cell are 4.27 m by 7.92 m (14 ft x 26 ft). The filter medium consists of No. 1 anthrafilt (anthracite coal) with grain sizes ranging from 0.6 to 0.8 mm. The uniformity coefficient of the particles is 1.75 and the medium depth is 0.68 m, (27-in). The medium is underlaid by 0.4 m (16-in) of graded supporting gravel. Each cell is backwashed at a rate of 0.26 $m^3/h/m^2$ (12.36 gal/min/sq ft), usually for about 7 minutes every 48 hours.

The backwashing schedule was changed on March 1, 1979. Thereafter, the filters were backwashed every 10 days or whenever the headloss reached 8 feet, whichever occurred first (42). The washwater is reclaimed and returned to the upflow basin influent. After filtration, the water flows to the clearwell. Chlorine gas for disinfection and fluoride for prevention of dental caries are added to the clearwell.

Water flows from the top of the aerator through the entire plant by gravity. From the clearwell, the water must be pumped to an 11, 350 cubic meter (3 MG) ground storage reservoir by three low-head pumps. Three high-lift pumps deliver the water from the reservoir to the distribution system.

The usual dosages of the chemicals added are:

Lime	90 mg/l
Alum	10 mg/l
Carbon dioxide	6.18 mg/l
Chlorine	2.25 mg/l
Fluoride	1.0 mg/l