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ADSORPTION KINETICS
FOR THE REMOVAL OF SOLUBLE MANGANESE
BY OXIDE-COATED FILTER MEDIA

by

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(ABSTRACT)

This study was conducted to examine the kinetics of manganese sorption on oxide-coated filter media. Initial experimentation confirmed the findings of other investigators; the Mn^{2+} sorption capacity of oxide-coated media increases as solution pH increases. Further study revealed that uptake rate kinetics could be described by first order kinetics and also increased with increasing solution pH. The addition of free chlorine ($HOCl$) to solution greatly enhanced Mn^{2+} uptake rate kinetics. Later studies indicated that the oxide coating had very little impact on the physical properties of the media tested.

Actual data from a water treatment plant filter confirmed laboratory experimental results by showing that sorption of soluble manganese does indeed occur on oxide-coated filters. The water treatment plant data also suggested that the sorption kinetics were relatively rapid, again upholding laboratory findings.

Results from the manganese kinetics and sorption experiments were combined to formulate a theoretical model

which would predict manganese breakthrough in a filter, given a known set of loading parameters. Preliminary use of the model indicated that oxide-coated filters could sorb ~~significant~~ quantities of soluble manganese before detectible levels of manganese appear in the effluent.

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INTRODUCTION

Manganese is found in widely varying concentrations in surface and groundwater sources throughout the United States. Aerobic or oxidized environments often yield soluble manganese concentrations of less than 0.05 mg/L, with the predominant species being $\text{MnO}_x(\text{s})$ precipitates. However, soluble manganese concentrations can exceed 1.0 mg/L in the reduced environment that typically exists in groundwater and reservoir hypolimnions. The concern over elevated concentrations of manganese in finished water supplies is based on aesthetic issues associated with water and plumbing fixture discoloration. To help minimize these problems, many states have implemented a secondary maximum contaminant level (SMCL) of 0.05 mg/L for manganese.

At most water treatment plants, soluble manganese is removed from water by the process of chemical oxidation. Potassium permanganate, added either alone or in conjunction with free chlorine, is probably the most prevalent oxidant used. Chemicals used less frequently include ozone and chlorine dioxide. Chemical oxidation as a means of removing soluble manganese is usually a very efficient process; however, impacts due to competitive oxidant demand, temperature, and solution pH have been noted.

To avoid the expense required to implement and maintain chemical oxidant addition (chemicals and sedimentation

basins), many small water treatment plants (flows <2 MGD) have opted for the use of manganese greensand. Manganese greensand is a naturally occurring zeolite which, when operated in a columnar fashion, serves to oxidize and precipitate out Mn^{2+} , Fe^{2+} , HS^- , and other reduced forms of compounds that are found in raw water sources.

Manganese greensand columns can be operated in either a continuous or intermittent regeneration mode. In the first situation, the column need not be shut down for regeneration, as is the case with the latter.

Recent investigations have revealed that the same oxide coatings present on manganese greensand can also be found on the filter media that comprises mixed-media filtration systems. Preliminary studies have shown that these coatings have a significant capacity for the removal of soluble Mn^{2+} from solution. The uptake rate reported was rapid, however, quantitative rate data have yet to be developed.

This research thesis was initiated to provide further information related to the potential for Mn^{2+} removal within oxide-coated, mixed-media filters. Specific objectives were as follows:

1. Quantify the amount of oxide coating present on filter media collected from a variety of full-scale treatment facilities;
2. Determine the maximum adsorption capacity of $\text{MnO}_x(\text{s})$ surface coatings for removing Mn^{2+} from solution,

emphasizing the effect of solution pH on removal capacity;

3. Quantify the kinetics of Mn^{2+} removal as a function of surface oxide coating concentration and solution pH;
4. Determine the effect of the presence of free chlorine on the kinetics of Mn^{2+} uptake by oxide-coated filters; and,
5. Determine whether the presence of an oxide surface coating has significant impacts on the physical characteristics (effective size, uniformity coefficient, and solid density) of filter media.

LITERATURE REVIEW

This chapter presents background information on manganese chemistry, manganese greensand, surface chemistry of manganese greensand and manganese dioxide, and research done in the field of manganese sorption on manganese dioxide surfaces.

Manganese Chemistry

Oxidation States. In an aqueous environment, manganese can exist in the Mn(II), Mn(III), Mn(IV), Mn(VI), and Mn(VII) oxidation states. The Mn(II) and Mn(IV) oxidation states are the usual forms found in natural water. Manganese in the Mn(VII) oxidation state is a strong oxidant and, as such, is used in water treatment to remove reduced manganese.

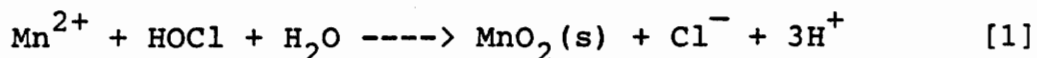
Oxidized manganese precipitated from water is normally represented by the stoichiometric formula $\text{MnO}_2(\text{s})$, known as manganese dioxide. However, investigators have found that this solid actually varies from $\text{MnO}_{1.1}$ to $\text{MnO}_{1.95}$, and is usually represented as $\text{Mn}_3\text{O}_4(\text{s})$. These formulae are not referencing a manganese with fractional oxidation states but rather a solid that is oxygen deficient (1).

Conventional Removal of Manganese. Removal of manganese from raw water sources is accomplished by oxidizing it from soluble Mn^{2+} to the solid $\text{MnO}_2(\text{s})$. This

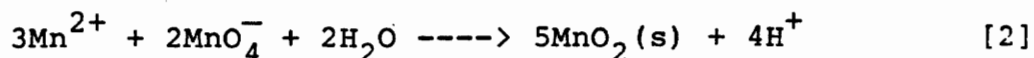
is typically done through the use of chemical oxidants.

Early attempts at manganese removal included aeration processes using oxygen as an oxidant, followed by detention and filtration (2). However, the kinetics of Mn^{2+} oxidation by $\text{O}_2(\text{aq})$ are very slow for pH values less than 9.5. In fact, to achieve 50 percent removal from a 0.55 mg/L soluble manganese solution at 25 degrees Celsius and a pH of 9.5 takes several hundred minutes (3).

Potassium permanganate and chlorine have often been used to promote manganese oxidation. Chlorine, when used as the sole oxidant of choice, can be an efficient oxidant if used under alkaline pH conditions ($\text{pH} > 8.0$) (4). It is also effective when used in conjunction with other oxidants to reduce chemical costs. Equation 1 shows the reaction that occurs during chlorine oxidation of soluble manganese.



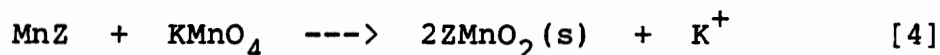
Potassium permanganate, used either alone or in conjunction with free chlorine, is the most frequently employed chemical for the oxidation and subsequent precipitation of soluble manganese. The following equation shows how potassium permanganate reacts with soluble manganese.



Although it is expensive, potassium permanganate is a rapid oxidant for Mn^{2+} and is operable over a wide range of pH conditions (4).

Manganese Greensand

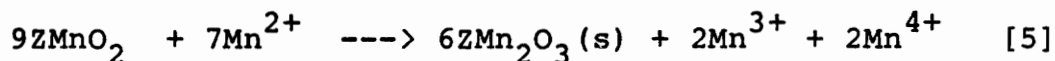
Greensand Zeolite. Greensand is the common trade name for the mineral glauconite. The name comes from the green appearance and granular nature of the mineral when it is dry. Originally used in water softening processes, greensand is sometimes used today at small groundwater treatment facilities (<2 MGD) for the removal of manganese and iron. Greensand is processed in alternating steps using manganous sulfide and potassium permanganate to produce manganese greensand. Partial reactions representing the steps are as follows:



where NaZ is the greensand (glauconite) and ZMnO_2 is the manganese greensand. After being processed, the greensand loses its green color and turns black due to the precipitation of manganese dioxide onto the surface.

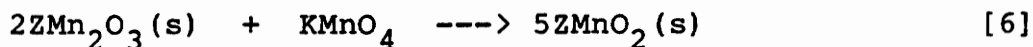
When soluble manganese (Mn^{2+}) passes through the greensand, it is sorbed to the surface and oxidized by the zeolite.

The process can be summarized by the following equation:



Greensand is therefore beneficial for soluble manganese removal because it both sorbs and oxidizes manganese (5). In addition, the granular nature of greensand provides an ideal precipitation site for the higher oxides of manganese represented in Equation 5 which are insoluble forms (6).

The capacity of a greensand filter is about 0.09 lb of manganese per cubic foot of greensand (5). Like any filter or ion-exchange column, breakthrough of soluble manganese occurs when the greensand filter becomes exhausted. Exhaustion takes place because the filter has lost its oxidative abilities, but this can be prevented by using potassium permanganate as a filter regenerant. The following equation describes how greensand media is regenerated:



An important difference in greensand filter regeneration from regular filter backwash/regeneration is that manganese remains in the greensand filter throughout the regeneration process. Instead of removing the manganese from the filter, the lower oxides are oxidized to higher

oxides, thus restoring the catalytic properties of the greensand bed (5).

Greensand Filtration. Greensand columns are operated either in the absence or presence of a chemical oxidant feed solution (termed intermittent and continuous regeneration, respectively). Either method, when implemented correctly, produces an effluent with manganese concentrations around 0.01 mg/L (6,7). Usually, potassium permanganate and/or free chlorine are used for the regeneration of the greensand media (6,7). A discussion of intermittent and continuous greensand regeneration follows.

Intermittent regeneration. When greensand media was first used in water treatment plants, intermittent regeneration was the preferred method of operation. As the name implies, regeneration is performed after the filter has operated for a certain length of time. The process consists of stopping the filtration cycle, washing the media with a dilute (0.5% - 1.0%) solution of potassium permanganate to reoxidize the surface of the media, and backwashing the media to remove any lingering particulate solids. The typical length of time required to complete these tasks is 1 hour.

Since oxidation of the soluble manganese occurs within the filter media, head losses are minimal. However, there is a drawback to this method of regeneration. Since the soluble manganese is oxidized on the media

surface, the media particle size continuously increases. This increase in media size, and subsequent increase in bed depth, must be taken into account when designing a greensand filter to operate in the intermittent regeneration mode (6,7).

Continuous regeneration. As suggested by the name, continuous regeneration results in the media being constantly reconditioned. The oxidative capacity of the bed is therefore exhausted at a relatively slow rate. In addition, a high percentage of the soluble manganese is oxidized before reaching the filter, either by potassium permanganate alone or in combination with chlorine. Chlorine addition reduces the amount of permanganate needed for regeneration and thus reduces the cost of the process (7).

In this process of manganese removal, the filter serves as a "last line of defense". When the oxidant doses are too small to adequately oxidize the manganese, the greensand filter sorbs and oxidizes the excess manganese. If, however, the oxidant doses exceed the demand required to oxidize the manganese in solution, the filter reduces the excess oxidant before it escapes in the effluent (6,7).

Since the greensand filter removes particulate matter, backwashing is needed when the headloss becomes prohibitive. To reduce the rate of headloss buildup, a 1-foot layer of anthracite is often placed on top of the greensand filter to

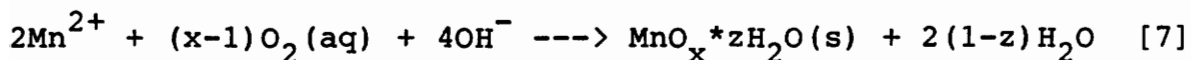
help catch any fine particulates that might otherwise clog the greensand media (5-8).

Surface Chemistry

Catalytic Properties of Greensand. The oxidation process that occurs with a greensand filter is similar to the oxidation of soluble manganese through the use of chemicals. Therefore, this process may be considered a property of the manganese in its intermediate oxidation states rather than that of the greensand. The greensand media serves only as a site on which this process can take place (5).

The autocatalytic properties of greensand are produced by the n-type, extrinsic, semiconductive properties of the oxygen-deficient manganese dioxide crystal that is formed and precipitated. The lack of oxygen atoms on the precipitant results in vacancies that increase the conductivity of the manganese electrons to the surface of the crystal. These electrons promote ionization of oxygen on the surface, and in turn, the oxygen is held onto the manganese surface. The presence of this oxygen enhances the manganese oxidation reaction. When the surface becomes fully oxidized to MnO_2 , no further autocatalytic oxidation occurs and regeneration is required (5).

The equation representing the autocatalytic oxidation of soluble manganese is as follows:



When the dissolved oxygen concentration is between 1 mg/L and 10 mg/L, the reaction is zero order with respect to oxygen (5).

Manganese Dioxide Surface Properties. As mentioned previously, oxidized manganese is usually represented in the form MnO_2 , but the solid is actually oxygen-deficient crystals of the form $\text{MnO}_{1.1}(\text{s})$ to $\text{MnO}_{1.95}(\text{s})$. Research by Graveland and Heertjes (1) showed that these solids are amorphous and colloidal by nature. They are believed to form the manganese component of the oxidized surface that exists on manganese greensand.

Studies by Morgan and Stumm (3) indicated that $\text{MnO}_2(\text{s})$ has an isoelectric point at a pH value of about 2.8. This is the pH value at which the surface charge of the oxide is essentially zero. At pH values greater than 2.8, the net surface charge is negative, whereas the surface charge is positive for pH values less than 2.8.

Investigators have also noted that when Mn^{2+} is sorbed initially by this oxidized surface, it displaces a H^+ ion. However, since the charge exchange process does not occur on

a one-to-one basis, the ability of the oxide to sorb Mn^{2+} is eventually hampered as the negative charge of the surface weakens (3).

Morgan and Stumm (3) quantified the relative uptake capacity and the strong dependency on solution pH in their evaluation of the surface Mn^{2+} removal capacity of $\text{MnO}_x(\text{s})$. As shown in Figure 1, the specific amount of soluble manganese uptake increases dramatically as the pH of the solution increases, especially with pH values greater than 6.5. This can be explained by the surface charge phenomena described earlier in this chapter. As the pH of the solution increases, the surface charge becomes more negative; thus, the capacity for the oxide surface to accept positively charged manganese increases. Research studies have shown that the oxide coatings present on manganese greensand also develop on the filter media present in mixed-media filters. Since many water treatment plants operate their mixed-media filters at pH values between 6.5 and 7.5, the data presented in Figure 1 could have major implications regarding the way these filters function for Mn^{2+} removal.

The "Natural Greensand" Effect

Knocke et al. (4) studied soluble Mn^{2+} removal on oxide-coated filter media from several full-scale water treatment facilities, ultimately characterizing the process

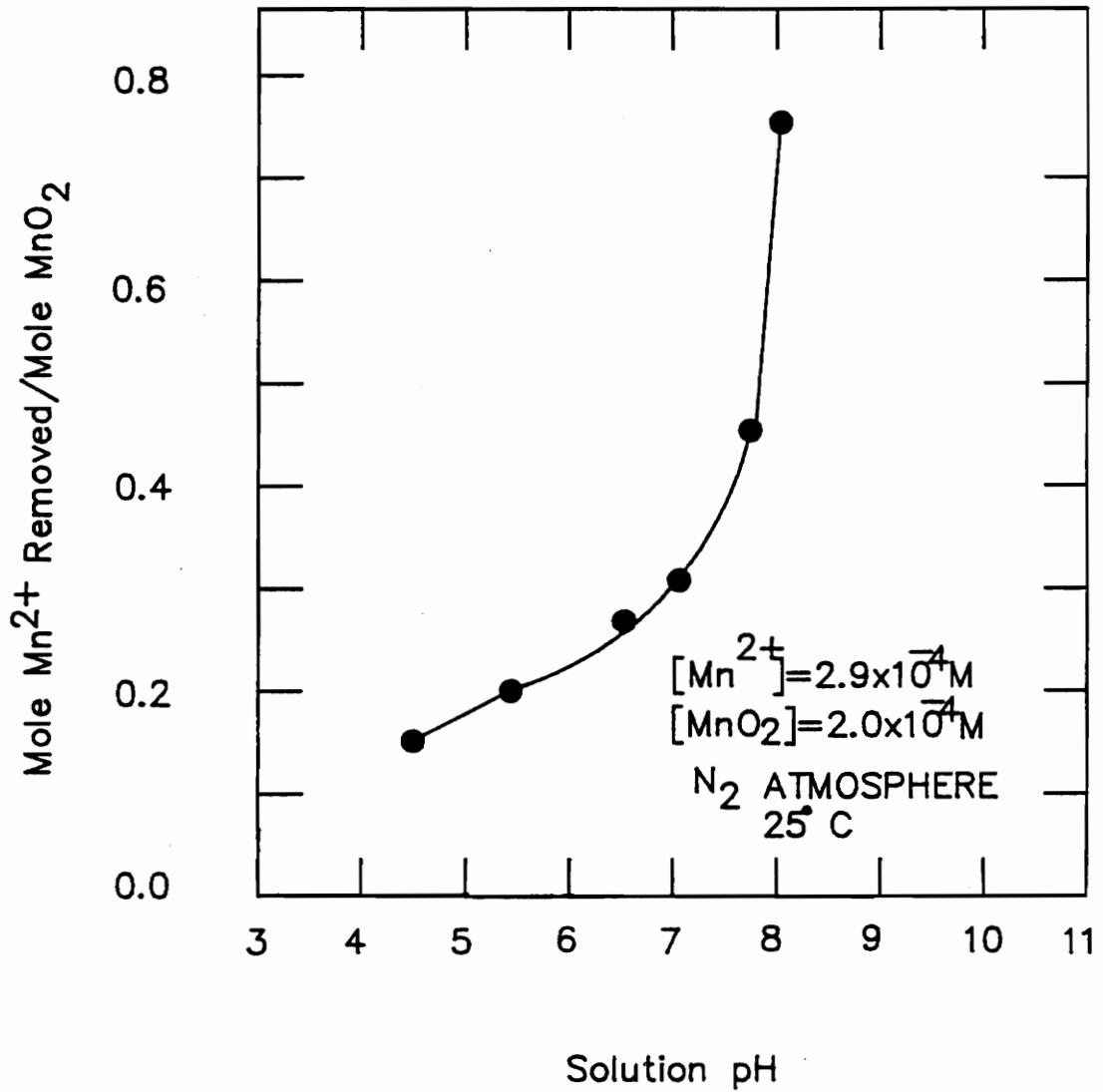


Figure 1. Impact of pH on sorption capacity of $\text{MnO}_2(\text{s})$ for Mn^{2+} removal (after Morgan (3)).

as a "natural greensand" phenomenon. The authors investigated the effects of a variety of parameters on Mn^{2+} removal and made the following conclusions/observations:

1. The uptake of Mn^{2+} by oxide-coated filter media was significantly affected by solution pH; typical results from their studies are included in Figure 2. Under acidic pH conditions, no uptake was observed in the absence of an oxidant such as $HOCl$ in the filter-applied water. However, under alkaline pH conditions, filters could be operated for extended periods of time without significant Mn^{2+} breakthrough.
2. The presence of free chlorine in the filter-applied water enhanced Mn^{2+} uptake, especially under acidic (pH 6.0-6.5) solution conditions. Representative results are shown in Figure 3. These results also suggested that the uptake was very rapid, as indicated by the fact that most of the observed removal took place in the upper 3 inches of a 24-inch-deep filter bed (data at 3-inch depth labeled "Top Port" in Figure 3).
3. Adding free chlorine to the filter-applied water did not result in rapid Mn^{2+} oxidation. Ultrafiltration testing by the authors indicated that more than

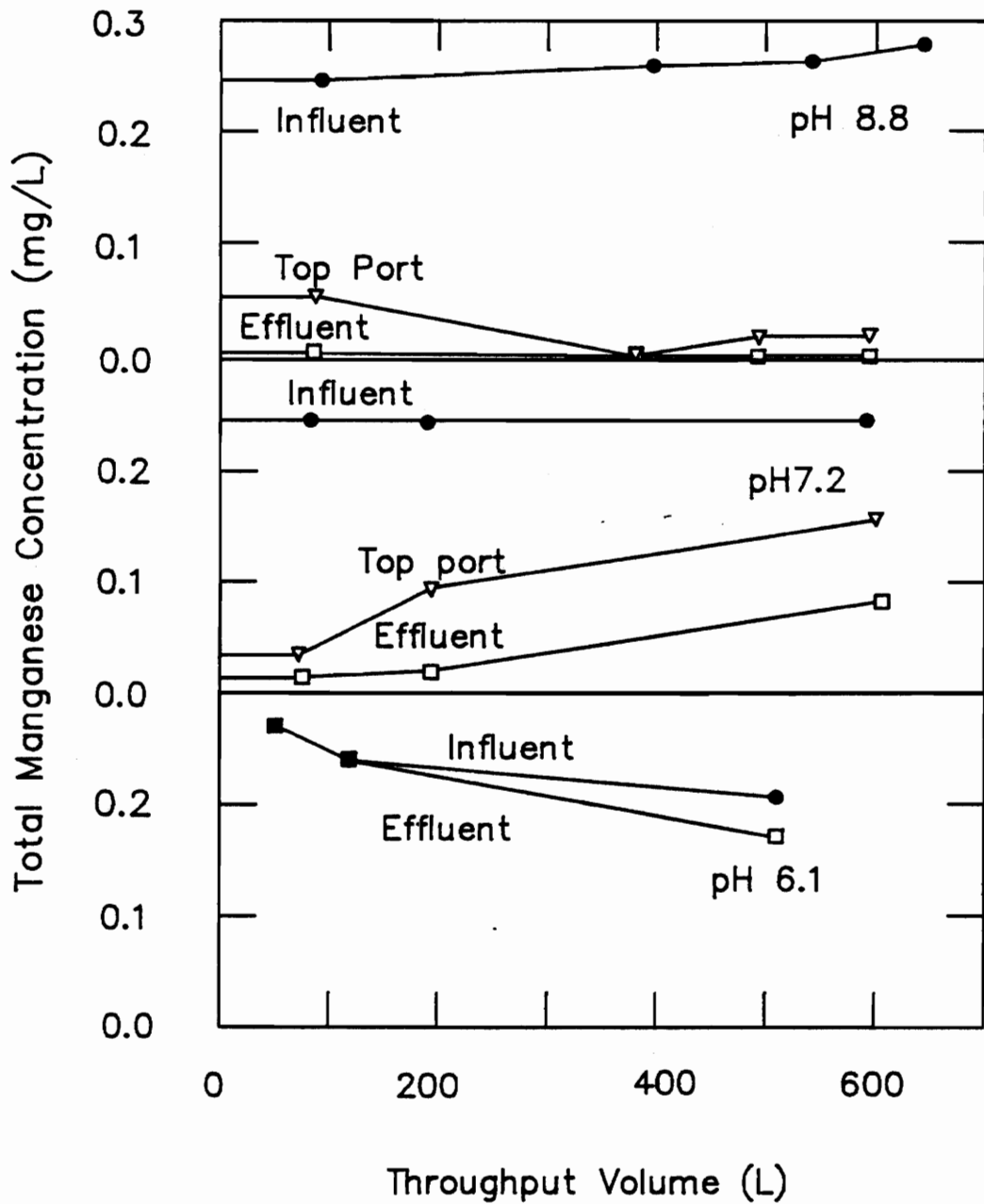


Figure 2. Effect of pH on the uptake of soluble manganese by oxide coated filter media. (No oxidant in filter – applied water; after Knocke *et al* (4)).

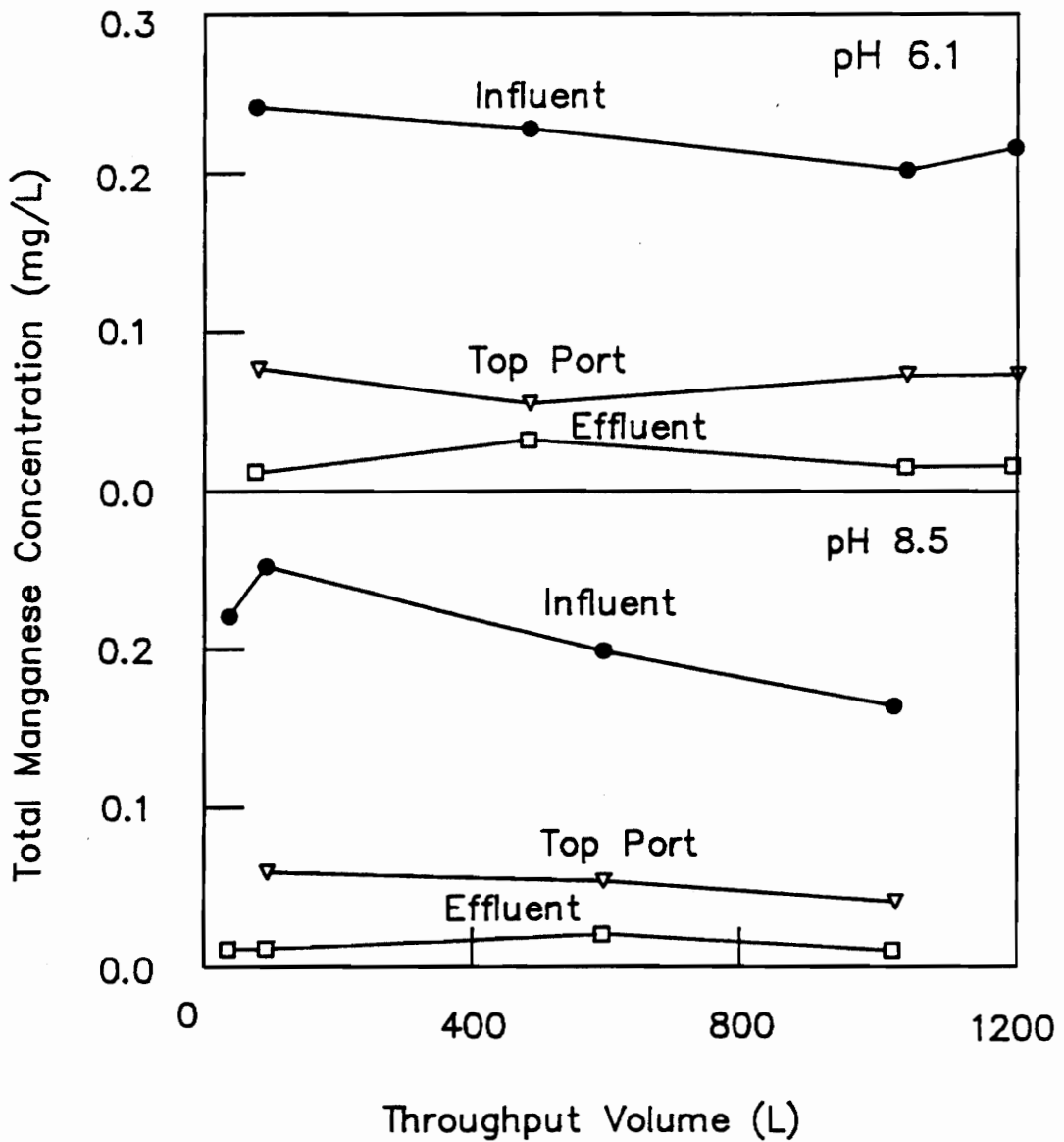


Figure 3. Effect of pH on the uptake of soluble manganese in the presence of chlorine during filtration. (HOCl concentration = 1.5–2.0 mg/L as Cl₂; after Knocke et al (4)).

98 percent of the manganese in the filter-applied water was present in the soluble Mn^{2+} species form. Given this lack of pre-filter oxidation plus the extended operation of the filter, the authors hypothesized that the $\text{MnO}_2(\text{s})$ surface catalyzed the oxidation of Mn^{2+} by free chlorine.

4. Stronger oxidants such as potassium permanganate, chlorine dioxide, and ozone oxidized the Mn^{2+} efficiently in the filter-applied water. When these oxidants were used, the major removal mechanism within the oxide-coated filter was physical capture of the colloidal $\text{MnO}_2(\text{s})$ formed during the pre-filter oxidation reaction.
5. Low temperature conditions did not impede the uptake of Mn^{2+} by oxide-coated filter media.
6. Soluble Mn^{2+} that was removed by the oxide-coated filter media in the presence of free chlorine was not released during filter backwashing. Instead, more than 90 percent of the manganese was retained on the surface of the filter media.

Summary

Prior research has clearly demonstrated the efficiency of $\text{MnO}_2(\text{s})$, either when present as manganese greensand or "natural greensand," in soluble Mn^{2+} removal. Unfortunately, limited quantitative kinetic data are available to describe the actual rate of Mn^{2+} uptake either in the presence or absence of a filter-applied oxidant such as free chlorine. The hypothesis of Knocke et al. (4) that the uptake was kinetically rapid was based on their observation that most Mn^{2+} removal occurred in the upper few inches of an oxide-coated filter. Likewise, Morgan and Stumm (3) observed in their batch sorption/uptake studies that equilibrium between soluble Mn^{2+} and surface-sorbed Mn^{2+} concentrations was typically reached in less than 2 minutes. The kinetics of Mn^{2+} removal by oxide-coated filter media as quantified by the research portion of this thesis, will be presented in subsequent chapters.

METHODS AND MATERIALS

Description of Media Used Throughout This Study

Various utilities throughout Virginia were contacted to solicit media samples from the filters used at their water treatment plants. Twelve of these utilities responded with samples, and one sample was acquired from the Williams Water Treatment Plant in Durham, North Carolina. The condition of each media sample was that of its state as it occurs during filter operation.

The filter media samples varied in composition, and included anthracite coal media, sand, or a mixture of sand and anthracite coal. Some media samples contained small amounts of gravel. Upon receipt, samples of the media were extracted and analyzed to determine the concentrations of manganese and iron. The extraction procedure was as follows:

1. A 4-gram sample of media and 100 mL of 0.5 percent nitric acid were placed in a 250-mL Erhlenmeyer flask. At least 25 mg of a strong reducing agent, hydroxylamine sulfate (HAS) was added and the solution was allowed to react for 2 hours. In this reaction, the manganese and iron found on the surface of each particular media were reduced and released into the acid solution.

2. The extractable surface amounts of manganese and iron were calculated through the use of Equation 8:

$$EMC = \frac{V * C}{W} \quad [8]$$

where:

EMC = extractable metal concentration (mg/g of media)

V = nitric acid volume used for extraction, L

C = extracted metal concentration in acid phase, mg/L

W = weight of media placed in Erlenmeyer flask with acid solution, g

A summary of the amount of surface iron and manganese found on the various media as well as a description of the media itself and its source is presented in Table 1. For comparison, Table 1 also lists values for unused anthracite coal, sand, and manganese greensand.

Description of Maximum Manganese Removal Capacity

The first series of experiments were performed to determine the capacity of each water treatment plant filter media for the uptake of soluble manganese, given a known amount of surface manganese oxide for each media and a known pH condition.

Table 1
Amount of Manganese Found on the Surface
of the Various Media Being Tested

Sample Number	Source	Media Type	Fe Concentration (mg/g media)	Mn Concentration (mg/g of media)
1	Roanoke	mixed	0.04	3.90
2	Lexington	sand	0.02	<0.01
3	Chesapeake	mixed	0.32	3.30
4	Petersburg	mixed	1.83	0.2
5	Norfolk	mixed	0.44	0.5
6	Portsmouth	coal	0.43	4.2
7	Rockersville	sand	0.15	1.2
8	Broadway	mixed	0.11	<0.01
9	Newport News	mixed	15.2	18.3
10	Woodstock	mixed	0.16	0.2
11	Durham	coal	0.50	60.0
12	Blacksburg	mixed	-	6.5
13	Ni River	mixed	-	6.7
		Mn greensand	0.75	4.3
		Virgin sand	0.26	<0.01
		Virgin coal	0.41	<0.01

NOTE: Mixed media refers to a mixture of sand and coal.

The manganese sorption capacity of each media was tested by passing a soluble manganese solution down through a filter column packed with the media. As shown in Figure 4, the experimental apparatus consisted of four 3/4-inch-diameter, Pyrex distillation jacket columns with 10 inches between the influent and effluent ports. The use of four columns allowed simultaneous testing of four different filter media at each pH condition. A 35-gallon holding tank was used to store the feed water, which was pumped by a Cole Parmer metering pump to the constant head tank. The tank ensured that the surface hydraulic loading rate would be maintained between 2 and 3 gpm/ft² throughout the uptake capacity studies.

The filter column feed water was prepared by first dechlorinating Blacksburg, Virginia, tapwater, adding the desired amount of soluble manganese, and adjusting the pH to the appropriate value. Dechlorination of the tapwater was deemed necessary because of the oxidative capabilities of the chlorine in the water. The feed water was prepared on a batch basis since the free chlorine content of the tapwater used in this study ranged from 0.3 mg/L to 1.3 mg/L as Cl₂. (The presence of combined chlorine was not expected in the feed water).

The chlorine content of the tapwater was measured by amperometric titration as described in Section 408C of Standard Methods (9), and an appropriate stoichiometric dose

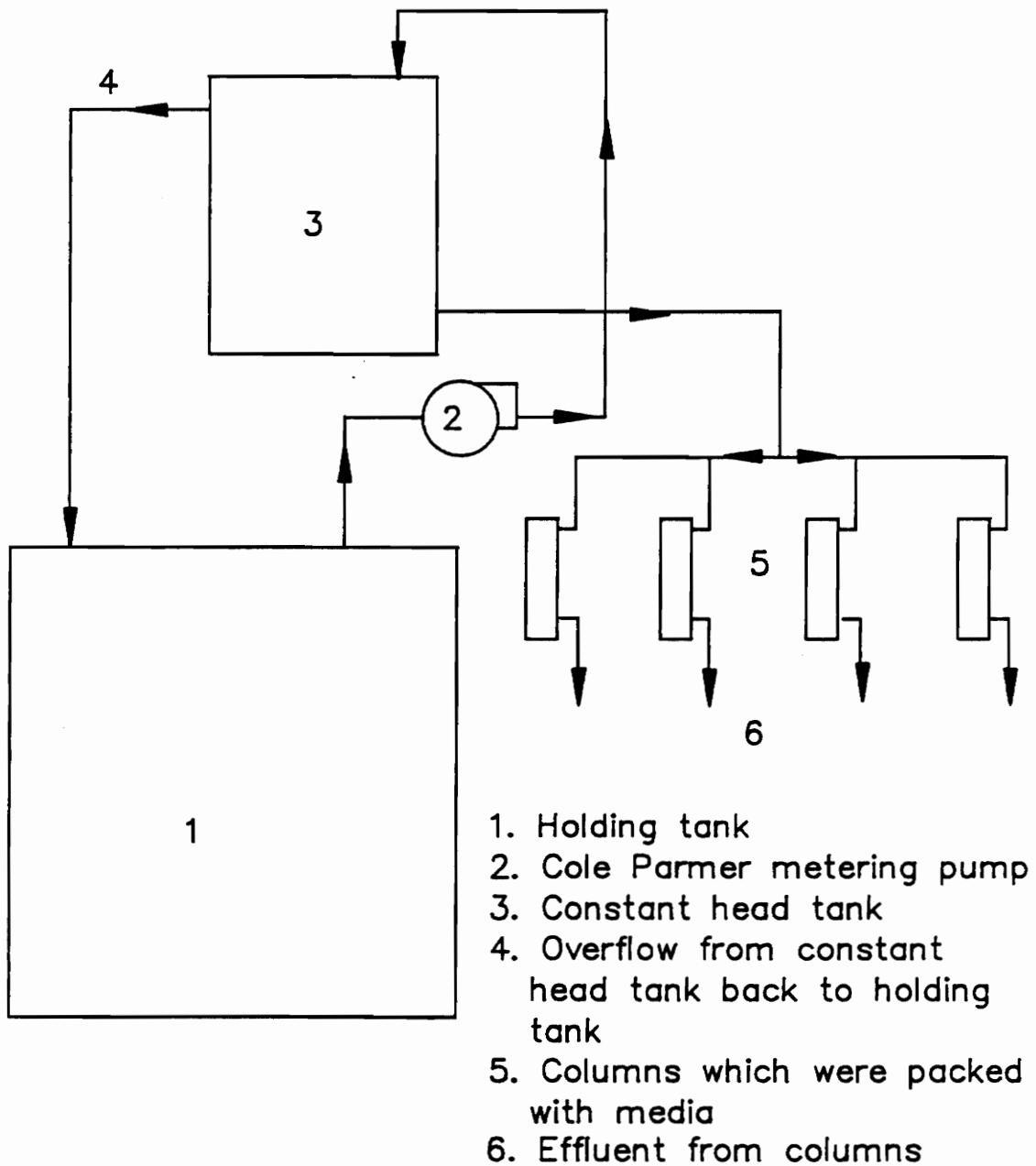


Figure 4. Schematic showing configuration of experimental apparatus used for capacity and kinetic studies.

of sodium thiosulfate was added to reduce the free chlorine that was present. Manganese was added to the water in the form of a manganous sulfate stock solution. The solution pH was measured by a Fisher Acumet pH Meter (Model 610) and, when necessary, adjusted by adding the proper quantity of concentrated nitric acid or sodium hydroxide.

Before being packed into columns, the surface manganese oxide coating on each media sample was completely oxidized to the $\text{MnO}_2(\text{s})$ phase to ensure consistency of the initial oxidation state for all tests. The filter media samples were "regenerated," or completely oxidized, by pumping a 2 percent by weight potassium permanganate solution through a column of media at a loading rate of 2.5 gpm/ft^2 for 1 hour. Distilled water was then pumped through the column to rid the surface of the media of any excess potassium permanganate. When the column effluent was observed to be clear (no visible evidence of potassium permanganate), the media was taken out of the column and allowed to dry for at least 12 hours before being repacked into the filter columns for testing.

Once the media had been oxidized and the soluble manganese solution had been prepared at the proper pH, the actual capacity study began. For the purposes of this investigation, maximum capacity or column exhaustion was considered to be the point when the effluent manganese concentration was equal to the influent manganese concen-

tration. The actual procedure for the manganese capacity study follows.

The soluble manganese solution was pumped through the various columns via the setup shown in Figure 4. Influent and effluent manganese concentrations as well as flow rates were monitored over time. A Perkin-Elmer Atomic Absorption Spectrophotometer was used to measure manganese concentrations throughout the study. This procedure is described in Standard Methods, Section 303 (9).

To determine the capacity of a particular column for the uptake of soluble manganese, effluent manganese concentration data were graphed as a function of total volume of water treated. An example of one such plot can be seen in Figure 5. The shaded region of the graph represents the difference between the influent and effluent manganese concentrations, and therefore the amount of soluble manganese taken up by the media. This information was used to mathematically determine the total soluble manganese uptake. For this example, the total amount of manganese removed was 167 mg.

When the maximum capacity of a particular column was reached, a permanganate demand test was performed on the media by passing a solution of potassium permanganate through the column. Permanganate demand, as used in this study, is defined as the quantity of potassium permanganate required to totally oxidize the filter media surface present in a column. A demand test ended when the influent and

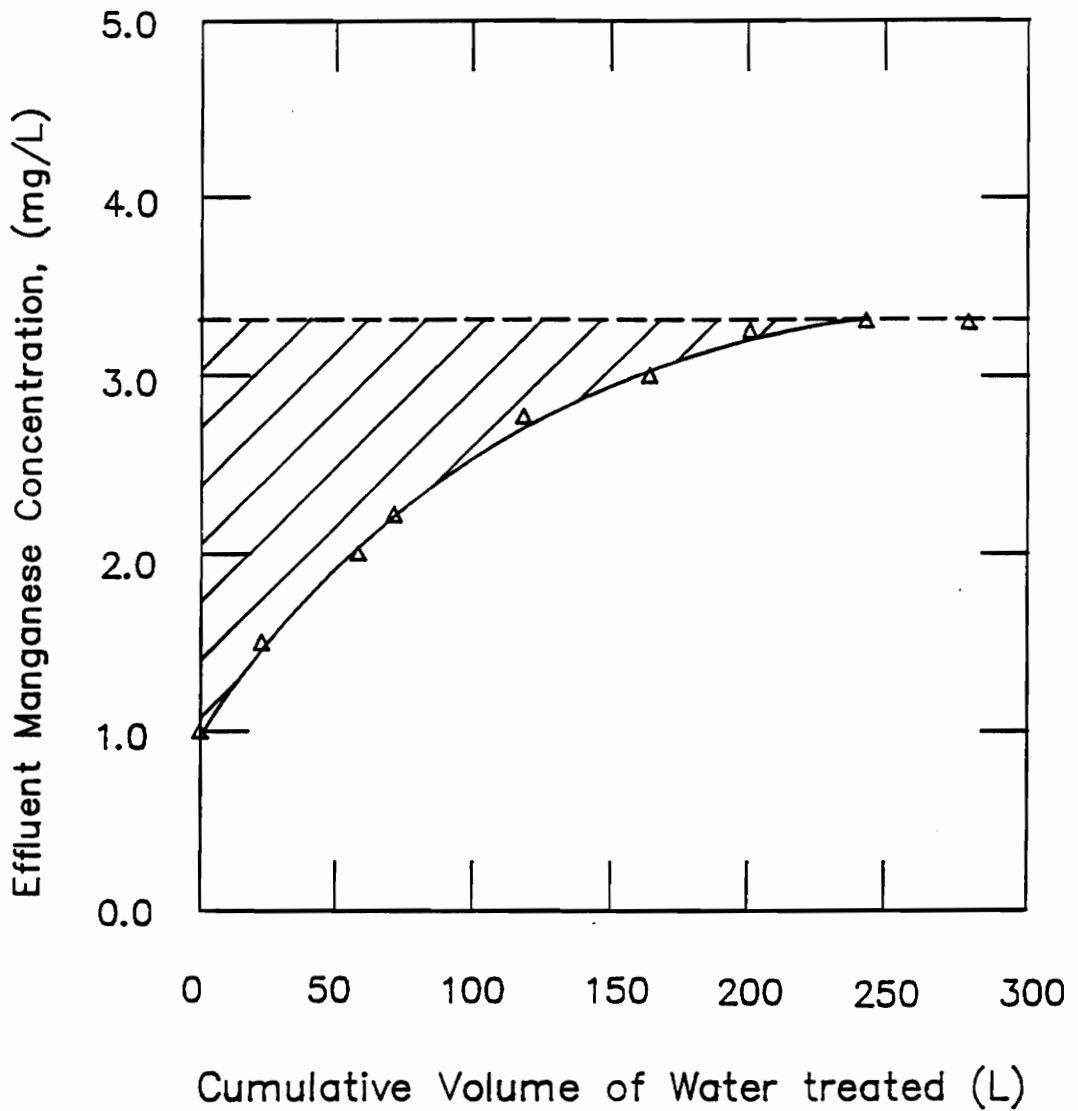


Figure 5. Manganese breakthrough curve for media 11 with an influent manganese concentration = 3.3 mg/L, an influent pH = 6.0, and a flow = 40 mL/min. (Hatched area represents amount of soluble manganese sorbed to media surface.)

effluent concentrations of potassium permanganate were determined to be analytically equivalent.

The desired strength of the permanganate regenerant solution was estimated by first converting the amount of Mn^{2+} taken up to milliequivalents, assuming all adsorbed Mn^{2+} must be oxidized to Mn^{4+} . This was balanced by a like amount of equivalents of potassium permanganate, which were calculated on the basis of Mn^{7+} being reduced to Mn^{4+} . Through this calculation, an anticipated equivalence demand for potassium permanganate was determined.

After calculating a theoretical demand, a concentration of potassium permanganate solution was chosen which, when fed at a flow rate of 2.5 gpm/ft², yielded a titration curve that lasted approximately 1 hour. Also, preliminary experiments were conducted that indicated the measured permanganate demand of an oxide-coated media was not affected by the potassium permanganate regenerant concentration range at least for potassium permanganate concentrations between 100 mg/L to 500 mg/L as Mn.

Potassium permanganate concentrations were determined by using a Fisher-Porter amperometric titrator in a procedure developed by Carlson (10). This procedure is described below.

A known volume of the permanganate solution sample (typically 2 mL to 5 mL) was diluted with distilled water to a final volume of 200 mL and a few drops of pH 7 buffer and

1 gram of potassium iodide were added. The amperometric titrator was placed on the "total" setting and the titration was performed using phenol arsene oxide (PAO) as the titrant. The sample was titrated until the detection needle on the amperometric titrator failed to deflect to the left (signaling the end of the titration). The volume of titrant required for each sample was measured and substituted in Equation 9 to determine the concentration of the permanganate solution.

$$\text{KMnO}_4 \text{ (mg/L as Mn)} = \frac{(N_{\text{PAO}}) (V_{\text{PAO}}) (54.9)}{V_1 (n_1)} \quad [9]$$

where:

N_{PAO} = normality of PAO titrant solution (usually .00564 eq/l)

G = gram atomic weight of manganese (54.94×10^3 mg/mole)

V_{PAO} = volume of PAO titrant (L)

n_1 = number of equivalents transferred per mole (reported as 3.5 by Carlson)

V_1 = volume of KMnO_4 sample prior to dilution with distilled water (L)

By substituting in the various constants above, Equation 9 becomes:

$$\text{KMnO}_4 \text{ (mg/L as Mn)} = 88.5 \frac{V_{\text{PAO}}}{V_1} \quad [10]$$

The actual permanganate demand of the oxide-coated media was found by plotting effluent concentrations of permanganate versus time in a manner similar to the manganese breakthrough curve shown in Figure 2. The amount of permanganate used in the demand test then could be calculated by determining the mass area between the influent and effluent concentration lines.

Kinetic Studies

All kinetic studies were conducted using the same experimental procedures. One group of experiments was performed with free chlorine (influent concentration ranging from 1-11 mg/L) present in the filter-applied water, while another group was conducted in the absence of any oxidant.

The various kinetic experiments employed the same column setup that was used in the media exhaustion studies. Four columns were set up with varying depths of media (ranging from 1 inch to 3-1/2 inches); each test was performed using the same media in all the columns. Each media was tested under pH conditions ranging from 5.5 to 7.9.

The depth of media as well as media mass were recorded for each column setup in the kinetic studies. Column depth was an important parameter; this value and the known diameter of the column (3/4 inches) were used to calculate the actual hydraulic detention time within each column. The detention times were calculated as follows:

$$t_d = \frac{d * A * \epsilon}{Q} \quad [11]$$

where:

- t_d = detention time of the solution in the column, (minutes)
- d = depth of the media in the column, (inches)
- A = cross-sectional area of the column (using inner diameter), (square inches)
- ϵ = porosity of the media in the column (estimated to be 0.42, typical for filter media)
- Q = flow of solution through column, (cubic inches/minute)

First-order decay reaction kinetics were used to analyze the data collected. The first order decay equation can be expressed as follows:

$$Mn_t = Mn_0 e^{-kt} \quad [12]$$

where:

- Mn_t = effluent manganese concentration (mg/L) at time, t
- Mn_0 = influent manganese concentration, (mg/L)
- k = uptake rate constant, (min^{-1})
- t = solution detention time in column (minutes)

The uptake rate constant values (k -values) were determined by plotting the natural logarithm of the effluent Mn concentration versus the corresponding column hydraulic detention time. These concentrations were equilibrium effluent concentrations. At each detention time, a column required a certain length of time to reach equilibrium, at which time the effluent concentrations became fairly

constant. In most cases, the time required to reach equilibrium was 2 hours. By plotting the $\ln[Mn_t]$ on the y-axis and the detention times in minutes on the x-axis, the slope represented the particular k-value with units (min^{-1}). An example of one such plot can be seen in Figure 6.

The range of influent manganese concentrations used in the kinetic study was 0.22 mg/L to 1.20 mg/L. However, the manganese concentration of the influent solution was held constant (0.45 mg/L for Media #7 and 0.77 mg/L for Media #1), for each set of tests in which the pH of the influent solution was varied.

Sieving Procedure

A sieve analysis was performed on various filter media samples to determine the extent to which a surface coating of manganese dioxide would affect average media particle size. A sample of each media was treated with HAS in one case and treated with a 2% potassium permanganate solution in the other case. Permanganate treatment of the media was performed in the same manner that was used to regenerate the various media for the capacity studies. HAS treatment, however, was performed on a "batch" basis. The media was placed in 2-liter beakers containing distilled water and HAS. After allowing approximately 4 hours for the HAS to react, the media was thoroughly rinsed with distilled water.

The permanganate regeneration of the media was performed to totally oxidize the surface of the media, and in

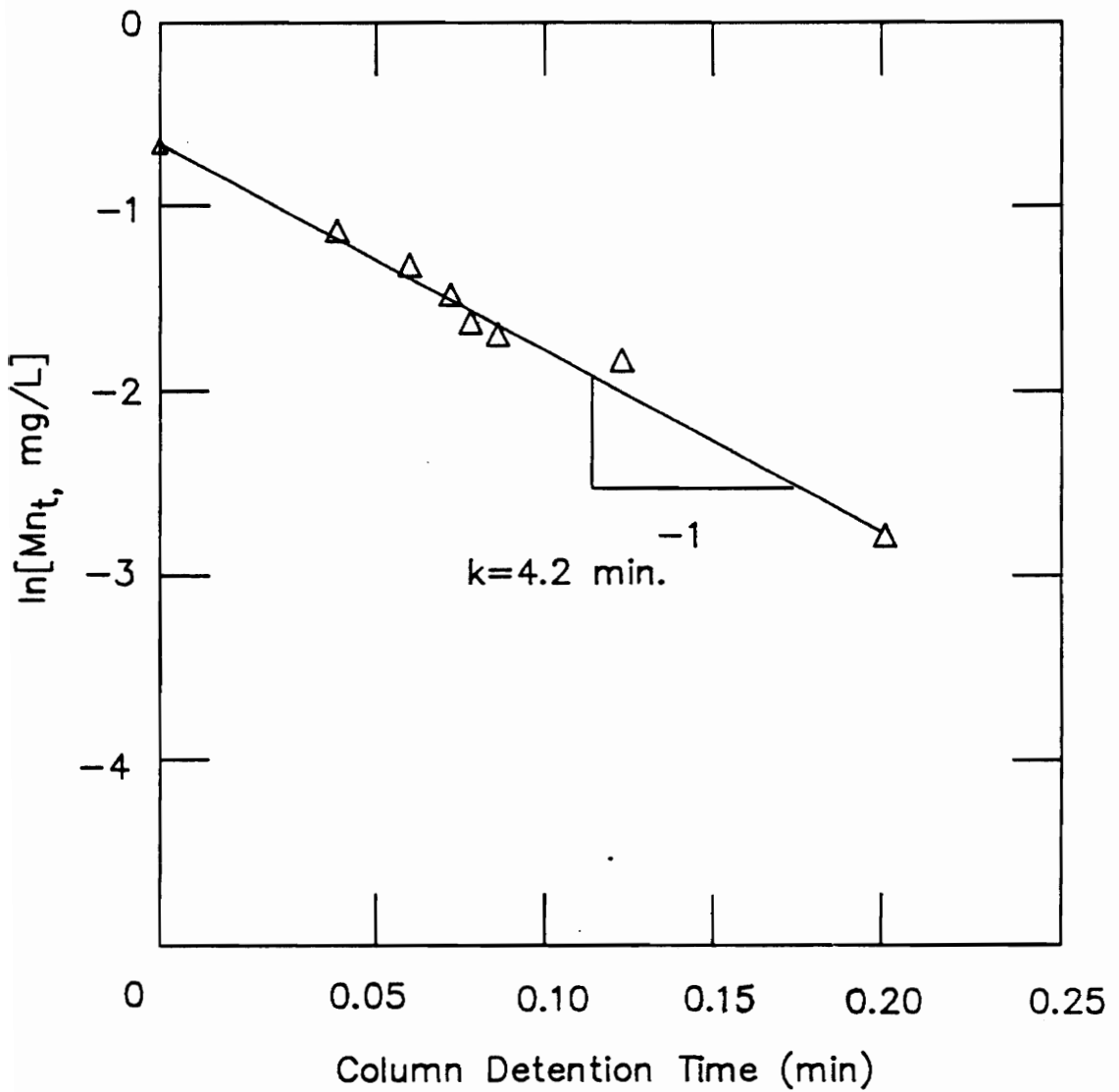


Figure 6. Representative effluent manganese concentration profile versus column detention time for Media #3 (influent pH = 7.1; no oxidant present)

so doing, maximize the solid manganese dioxide surface coating of the media. By treating the media with HAS, the surface coating was dissolved and totally removed.

Before sieving, all media was allowed to air-dry for 24 hours. The sieve analysis was performed as described in ASTM designation D422-63 (11). Using a 100-gram sample of media, the results were plotted on semi-log paper. Figure 7 shows the grain size distribution for one of the samples tested.

The effective size and Uniformity Coefficient (U.C.) were calculated for each media sample. As the term implies, the U.C. parameter is used to determine how uniform a particular media sample is with regard to the size of individual particles. The U.C. was calculated by using the following formula:

$$U.C. = \frac{D_{60}}{D_{10}} \quad [13]$$

where:

U.C. = uniformity coefficient

D_{60} = particle size for which 60% of the sample by weight is smaller.

D_{10} = particle size for which 10% of the sample by weight is smaller.

The effective size of the media was considered mathematically equivalent to D_{10} .

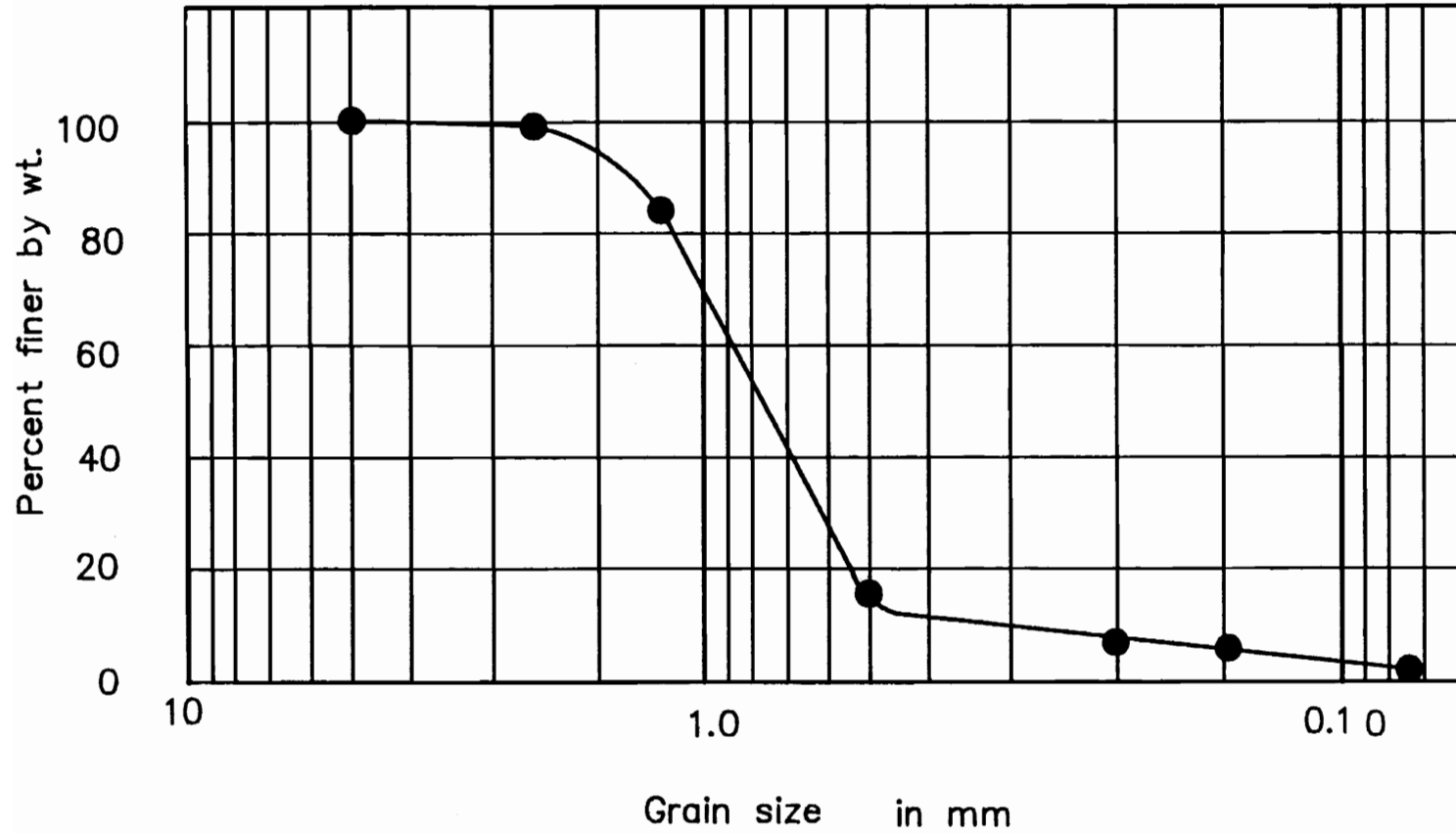


Figure 7. Grain size distribution for media #11 after hydroxylamine sulfate treatment

Specific Gravity Determination

The technique used to derive specific gravity involved a series of equations using measurements obtained from a pycnometer. The first step of the process required measuring both the dry weight of the pycnometer and the weight of the pycnometer filled with distilled water. The resultant values were substituted in Equation 14 to calculate the volume of the pycnometer:

$$V(p) = \frac{M(p) - M(pw)}{P(w)} \quad [14]$$

where:

$V(p)$ = the volume of the pycnometer
 $V(w)$ = the volume of water in the pycnometer with media
 $M(p)$ = the weight of the empty pycnometer
 $M(pw)$ = the weight of the pycnometer filled with water

The pycnometer was dried, filled to about the half-way mark with a media sample, and weighed. Distilled water was then added to the pycnometer and the total weight was measured. These values were used to determine the volume of the media sample as follows:

$$V(w) = \frac{M(pmw) - M(pm)}{P(w)} \quad [15]$$

where:

$V(w)$ = the volume of water in the pycnometer with media

$M(pmw)$ = the weight of the pycnometer filled with media and water

$M(pm)$ = the mass of the pycnometer with media

$P(w)$ = the density of water at STP

The results of Equations 14 and 15 were used to determine the volume of the media sample:

$$V(m) = V(p) - V(w) \quad [16]$$

where:

$V(p)$ = the volume of the pycnometer

$V(m)$ = the volume of filter media in the pycnometer

$V(w)$ = the volume of water in the pycnometer with media

The volume of the media sample was substituted in Equation 17 to calculate the specific gravity:

$$P(m) = \frac{M(m)}{V(m)} \quad [17]$$

where:

$V(m)$ = the volume of filter media in the pycnometer

$M(m)$ = the mass of the media in the pycnometer

$P(m)$ = the density of media

The above process was repeated as required to calculate the specific gravity for media in the totally oxidized condition (after permanganate regeneration), and in the extracted condition (after treatment with HAS).

EXPERIMENTAL RESULTS

This chapter presents the data collected during the experimental portion of this study and significant trends that were observed. Specific subsections will include the effect of pH on the adsorption capacity of $\text{MnO}_x(\text{s})$ to remove Mn^{2+} ; the effect of pH and presence or absence of free chlorine on the rate of Mn^{2+} uptake by oxide-coated filter media; and the impact of an oxide coating on the physical properties of filter media.

Adsorption Capacity of $\text{MnO}_x(\text{s})$ for Mn^{2+} Removal

Prior work by Knocke et al. (4) showed that significant Mn^{2+} removal capacity existed in many oxide-coated, mixed-media filters. However, the authors did not provide specific quantitative information on removal capacity or how this capacity would be affected by variations in treatment operating conditions. Morgan and Stumm (3) quantified the Mn^{2+} uptake capacity of pure $\text{MnO}_2(\text{s})$ under the conditions of relatively well-defined suspensions of manganese dioxide, but did not establish whether this oxide was the principal or only manganese oxide form on the surface of the filter media. Thus, additional study was warranted to estimate the potential capacity of Mn^{2+} removal by oxide-coated filter media and to the results reported by Morgan and Stumm (3).

The capacity for Mn^{2+} removal was quantified as a combined function of the amount of surface $\text{MnO}_x(\text{s})$ coating and solution pH. Figure 8 depicts a plot of uptake capacity as a function of pH for three oxide-coated filter media. The media shown contained 3.3, 3.9, and 60.0 mg of surface-extractable manganese per gram of filter media. The plotted results showed two apparent trends. First, the specific Mn^{2+} removal capacity was not a function of the amount of $\text{MnO}_x(\text{s})$ present on the filter media. This effect was anticipated because the removal capacity in Figure 8 was reported on the basis of uptake per unit weight of $\text{MnO}_x(\text{s})$. From a surface chemistry standpoint, however, the similar uptake capacity of the three media samples indicated similar oxides present on the media.

The second trend which is evident in Figure 8 is the increase in specific Mn^{2+} removal capacity of the surface $\text{MnO}_x(\text{s})$ coating as the pH of the solution increases. For comparison, the results of a previous manganese sorption study by Morgan and Stumm (3) were depicted as a dashed line on Figure 8. The results of this study compared favorably with the trend as observed by Morgan and Stumm.

Permanganate Demand Experiments. During the course of this study, an attempt was made to correlate the amount of soluble manganese adsorbed by oxide-coated filter media to the amount of permanganate needed to regenerate the filter column after its removal capacity was exhausted. A

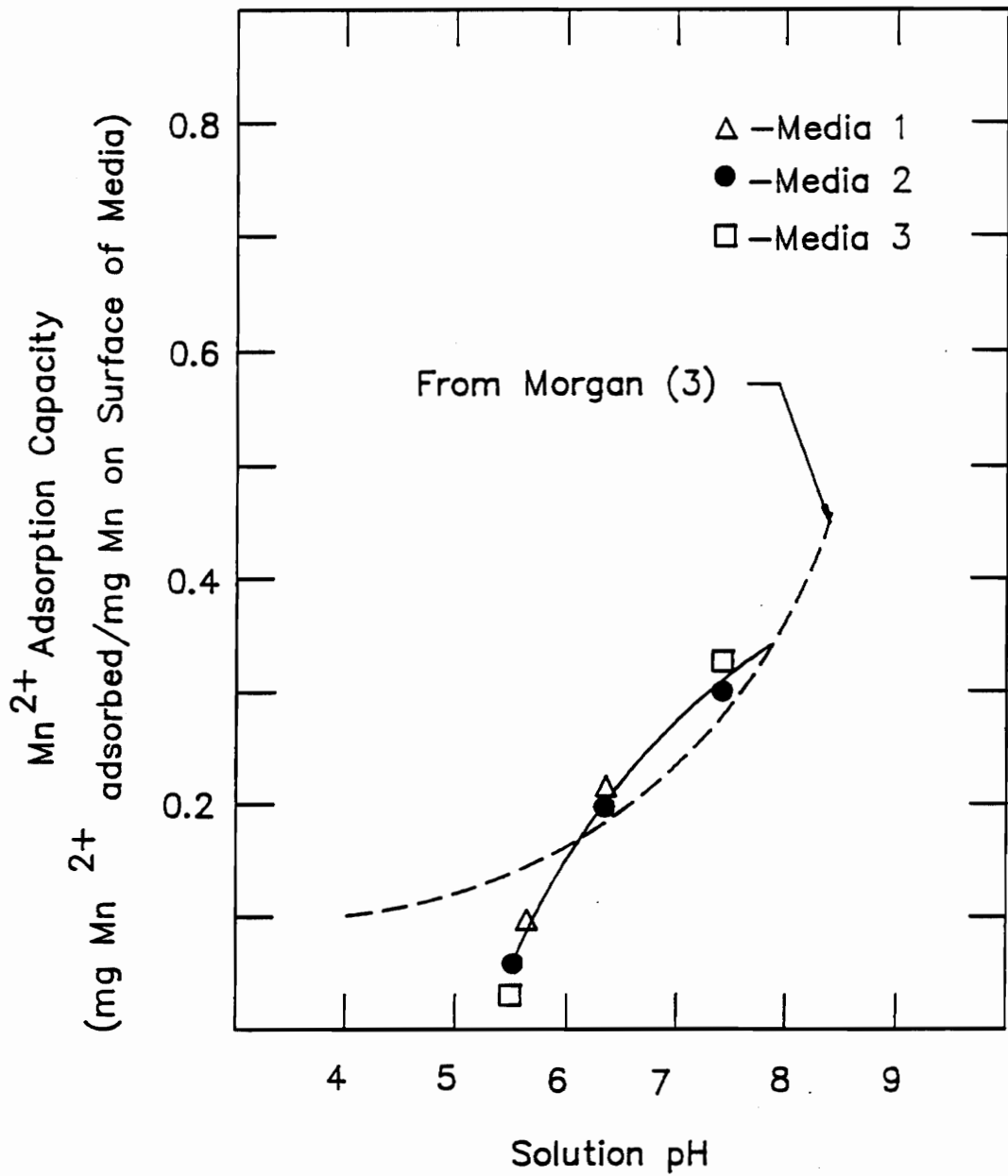


Figure 8. Mn²⁺ adsorption capacity of various oxide-coated media samples as a function of pH.

"theoretical" permanganate demand was calculated and compared to the actual permanganate demand determined through experimentation. Table 2 shows the results of laboratory analysis of the permanganate demand of various media after manganese sorption capacity studies were performed at the indicated pH.

In order to correlate the different media at various pH values, the amount of permanganate demand required was divided by the amount of soluble manganese which was sorbed to the media surface. The calculated figure was used as a normalized value for permanganate demand in the media comparison study. The results were highly variable at pH 6.0; closer agreement was obtained with increased pH conditions. Also, the apparent permanganate demand of the media seemed to increase slightly under the pH 7.5 condition.

The Effect of pH and Presence or Absence of Free Chlorine on Rate of Mn^{2+} Uptake by Oxide-Coated Filter Media

The first obstacle encountered in determining the reaction kinetics was how to describe the sorption of soluble manganese on an oxidized $MnO_x(s)$ surface in a filtration setting. By using the data compiled from five different Mn^{2+} uptake kinetic studies, uptake rate constants (k) were calculated for influent soluble manganese concentrations ranging from 0.20 to 1.20 mg/L (Table 3). First-order kinetics (Equation 12) were assumed. The

Table 2
Summary of the Ratio of
Observed Potassium Permanganate Demand (mg)
per Mass of Soluble Manganese Sorbed (mg)
for Various Media at Different pH Conditions

<u>pH</u>	<u>Media #</u>	<u>Amount of Mn²⁺ Sorbed (mg)</u>	<u>Permanganate Demand (mg KMnO₄)</u>	<u>mg KMnO₄ mg Mn²⁺ sorbed</u>	<u>Average</u>
6.0	1	13.8	25.7	1.86	1.02
	3	24.8	19.3	0.78	
	7	17.4	8.4	0.48	
	11	167	158	0.94	
7.0	3	16	15	0.92	0.94
	11	242	232	0.96	
7.5	1	5.6	6.9	1.24	1.30
	6	5.4	7.3	1.36	

Table 3
 Uptake Rate Constants Determined
 at Various Influent Manganese Concentrations
 (pH = 7.1, Media #1 tested,
 Amount of Manganese on Surface of Media
 = 3.90 mg Mn/g of Media)

Influent Mn conc (mg/L)	Residence Time of Solution in Column (min)	Eff Mn conc, (Mn _t) (mg/L)	Uptake Rate Constant, k (min ⁻¹)
0.20	0.05	0.19	4.8
	0.08	0.18	
	0.09	0.16	
	0.10	0.15	
	0.11	0.15	
	0.14	0.12	
	0.22	0.10	
	0.22	0.08	
0.30	0.12	0.19	4.8
	0.18	0.18	
	0.22	0.16	
	0.23	0.15	
	0.25	0.15	
	0.33	0.12	
	0.52	0.10	
0.45	0.11	0.31	4.1
	0.15	0.28	
	0.18	0.21	
	0.19	0.19	
	0.21	0.19	
	0.47	0.06	
0.8	0.09	0.59	5.7
	0.12	0.50	
	0.17	0.28	
	0.19	0.31	
	0.24	0.21	
	0.32	0.13	
1.20	0.08	0.90	5.0
	0.11	0.84	
	0.18	0.41	
	0.19	0.43	
	0.23	0.39	
	0.26	0.38	
	0.63	0.09	

calculated uptake rate constants were plotted as a function of the respective influent Mn^{2+} concentration (Figure 9). The resultant graph showed little variation in the uptake rate constant as a function of influent manganese concentration, confirming that the reaction is a first-order reaction which can be described by Equation 12.

Effect of pH on Uptake Kinetics. A series of experiments were performed to determine the effect of pH on uptake kinetics. Figures 10 and 11 show the effect of pH on uptake rate constants for two different media: Media #7 had a surface manganese oxide coating of 1.65 mg Mn/g of media, and Media #1 had a surface oxide coating of 3.3 mg Mn/g of media. The influent manganese concentration was held essentially constant at 0.45 mg/L (Figure 10) and 0.75 mg/L (Figure 11). In both tests, the Mn^{2+} uptake rate constant increased as solution pH increased.

Effect of Free Chlorine on Uptake Kinetics. Additional experiments were performed to determine effect of free chlorine on the kinetics governing Mn^{2+} sorption. As the free chlorine concentration increased, the uptake rate constant (k) also increased in an apparent linear fashion (Figure 12).

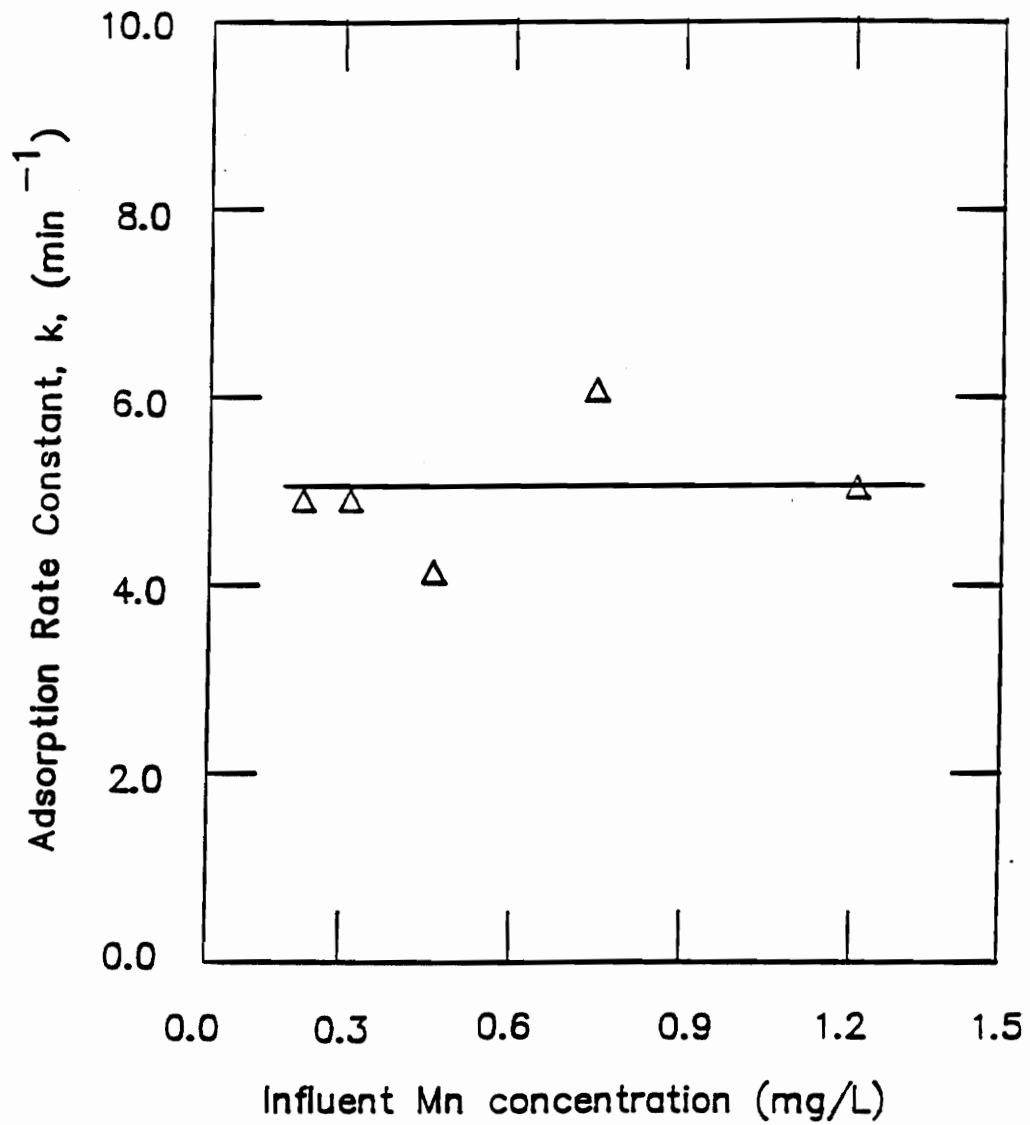


Figure 9. Influence of influent manganese concentration on uptake rate constant for media #1.
(pH=7.1, amount of manganese on the surface of the media =3.9 mg Mn/g of media.)

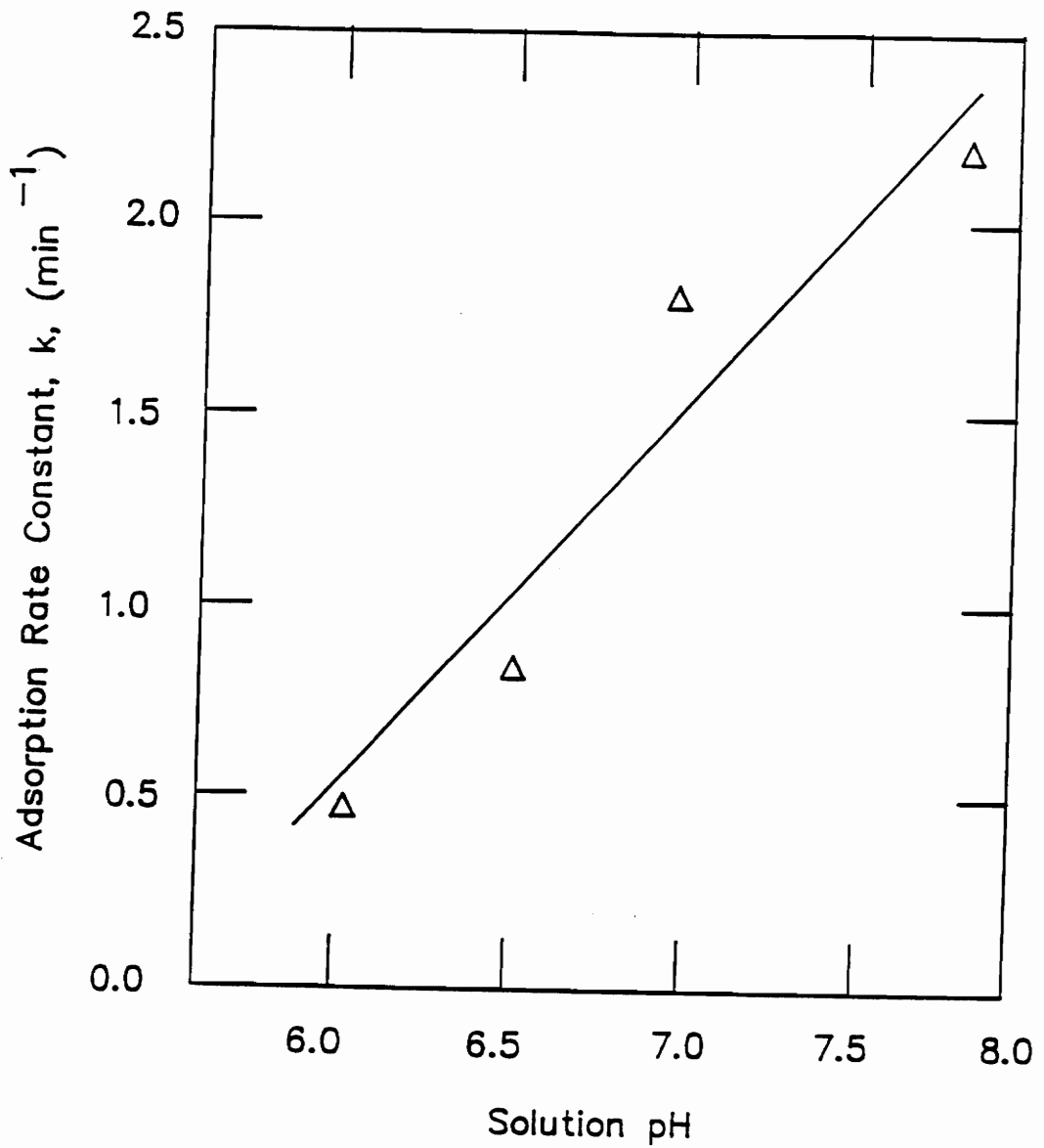


Figure 10. Influence of pH on uptake rate constant for media #7. (Influent manganese concentration = 0.46mg/L, amount of manganese on surface of media = 1.65mg Mn/g media.)

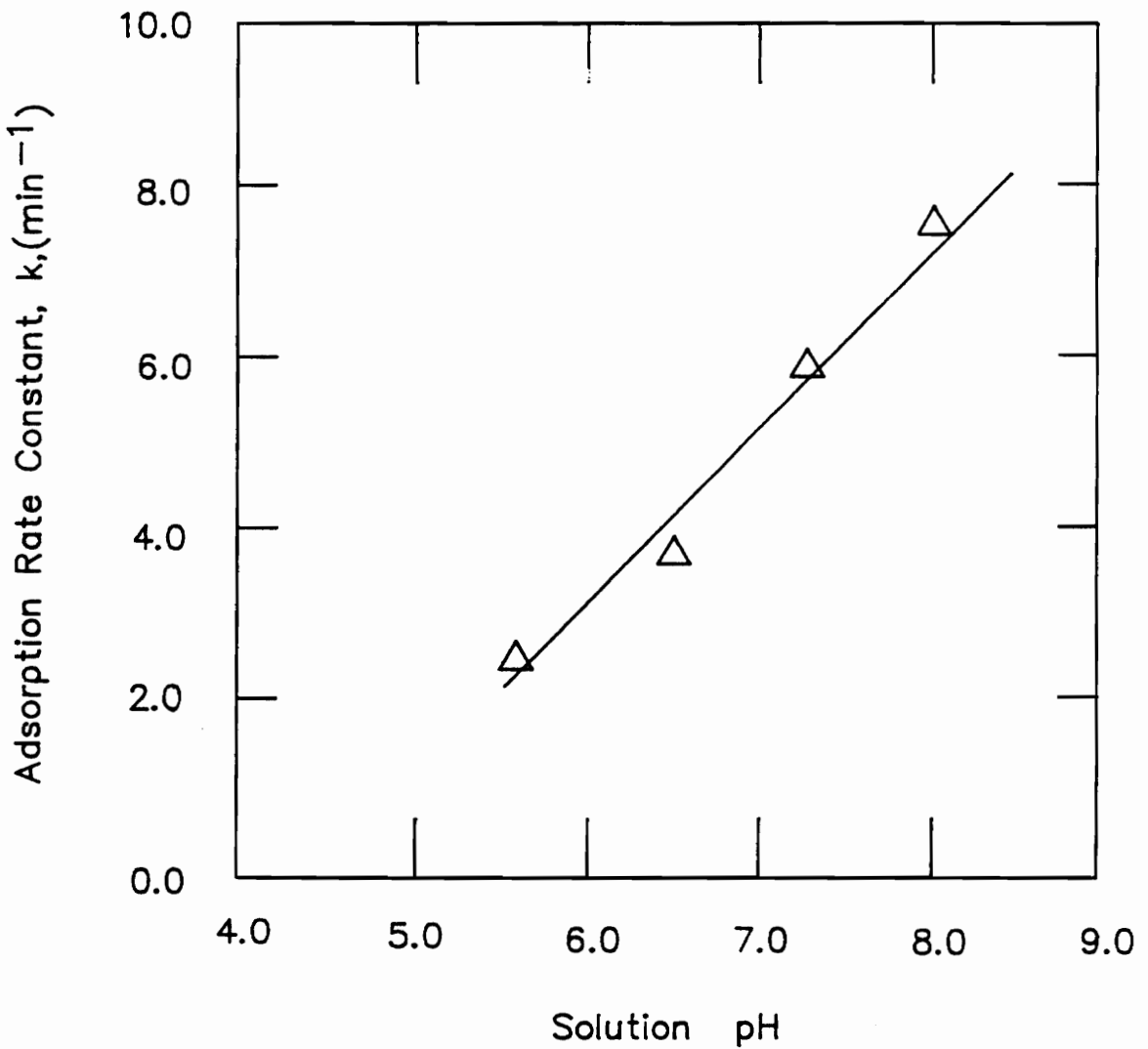


Figure 11. Influence of pH on uptake rate constant for media #1. (Influent manganese concentration = 0.77 mg/L; amount of manganese on surface of the media = 3.90 mg Mn/g of media.)

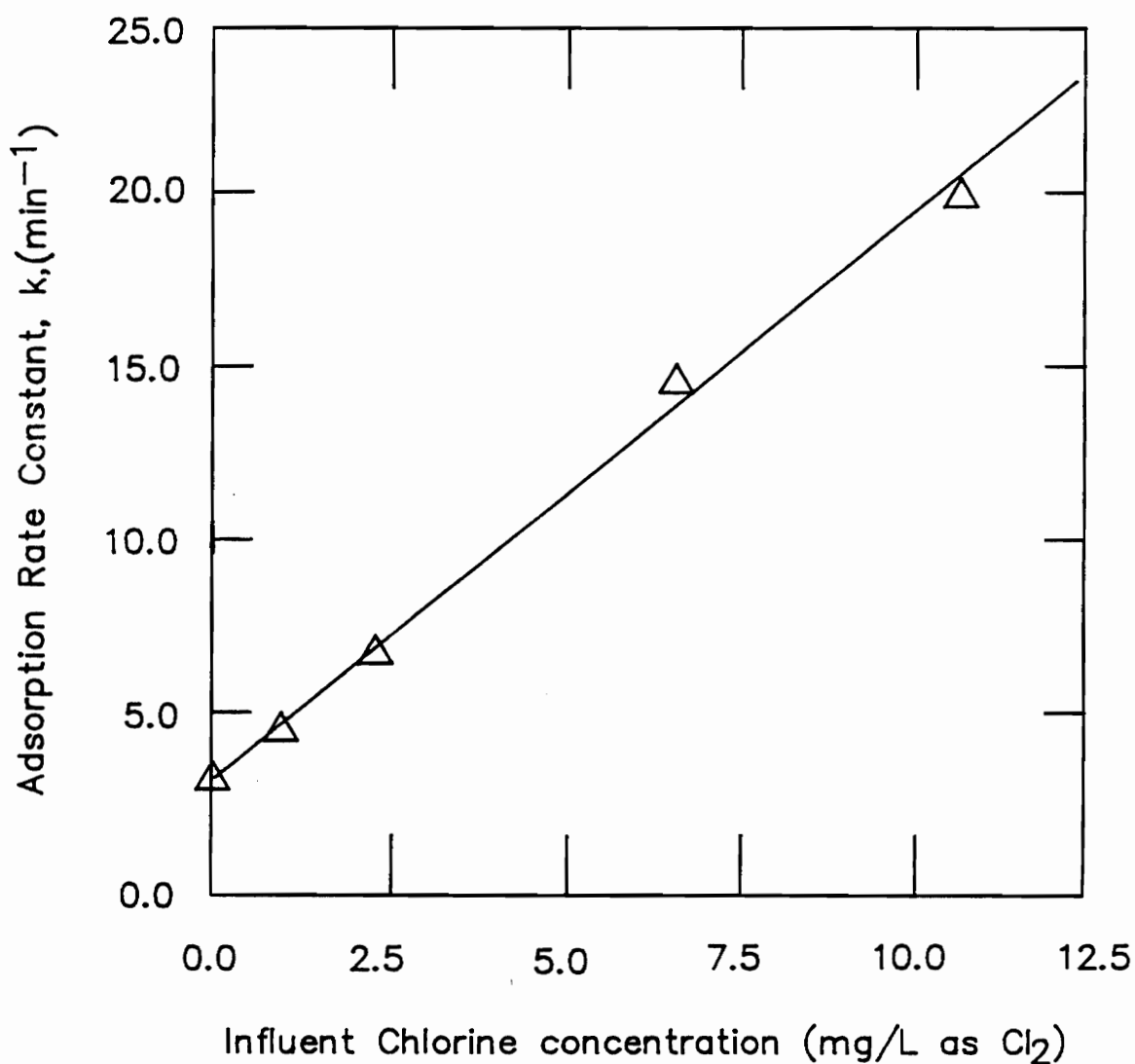


Figure 12. Influence of chlorine dose on uptake rate constant for media #1. (pH = 7.1; influent manganese concentration = 0.48 mg/L, amount of manganese on the surface of the media = 3.90 mg Mn/g of media).

Impact of Oxide Coatings on the Physical Properties of Filter Media

Studies were conducted to determine the effects on media size and density of an oxide coating on the surface of filter media. The size and density of samples of the same media in the coated state (oxide surface present) and in an uncoated state (no oxide surface present) were measured. The results of these experiments indicated that the presence of an oxide surface had little effect on the parameters listed for Media #6, #7 or #11 (Table 4). For comparison, the values usually encountered in typical water treatment plant filter media are also presented in Table 4.

Table 4
Results of Size and Density Studies
With and Without a Surface Coating
on the Media

<u>Media</u>	<u>Surface Coating</u>	<u>Specific Gravity</u>	<u>U.C.^a</u>	<u>Eff. Size^b (mm)</u>
Portsmouth (coal)	Yes	1.61	1.55	0.76
Portsmouth (coal)	No	1.59	1.60	0.74
Durham (coal)	Yes	1.90	1.82	0.55
Durham (coal)	No	1.95	1.88	0.48
Ruckersville (sand)	Yes	2.62	--	--
Ruckersville (sand)	No	2.64	--	--
Typical Values For:				
Sand ^c		2.65	1.35-1.75	0.40-0.55
Anthracite ^c		1.50	<1.70	0.45-0.80

^aUniformity Coefficient (D_{60}/D_{10})

^bEffective size (D_{10})

^cValues taken from Clark, Viessman, Hammer, Water Supply and Pollution Control, 3rd Edition, p. 391.

DISCUSSION

This chapter presents a discussion of the laboratory results, the effect of pH on the adsorption capacity of $\text{MnO}_x(\text{s})$ for Mn^{2+} removal, the effect of pH and presence or absence of free chlorine on the rate of Mn^{2+} uptake by oxide-coated filter media, and the impact of oxide coatings on the physical properties of filter media. Also, presented are the results from an extended filter uptake study, and suggested mathematical model to predict the behavior of a particular filter with regard to manganese sorption.

Adsorption Capacity of $\text{MnO}_x(\text{s})$ for Mn^{2+} Removal

The results of quantifying the adsorption capacity of an oxide-coated media for soluble manganese removal at various pH conditions (Figure 8) varied slightly from Morgan and Stumm (3). A possible explanation for this could be the method of generating the oxide surface. Morgan and Stumm produced manganese dioxide by using oxygen under high pH conditions to oxidize reduced manganese. The oxide surface used throughout the current study was formed by permanganate oxidation of reduced manganese on filter media. It is possible that the two methods of oxidizing manganese formed solids having slightly different surface characteristics.

In order to estimate the oxidation state of manganese in the surface oxide, a theoretically based plot was

developed. As shown in Figure 13, the plot illustrates the final oxidation state of the oxide surface manganese of a media after permanganate regeneration, given a known ratio of permanganate demand (mg KMnO_4) to sorbed manganese (mg Mn^{2+}). The plot suggested that as the ratio of observed permanganate demand-to-observed manganese sorbed increases, the final oxidation state of the oxide surface manganese becomes higher. The data summarized in Figure 13 and Table 2 infer that the end oxidation state of the oxide surface manganese after permanganate regeneration is between +3.3 and +3.6 for the pH range of 6.0-7.5.

Although the oxide surface formed in Morgan and Stumm's experiments, was apparently slightly different from the one formed in this study (+4 as opposed to between +3.3 and +3.6), the similar adsorption capacities of the two oxides suggests like adsorptive capabilities. Since the available data characterizing the oxide surface on filter media are insufficient, the Morgan and Stumm data may be considered a reasonable estimate on exhaustive capacity. Their experimental results could be used successfully for assessing the amount of uptake that might occur in a known mixed-media filter under given pH conditions.

Permanganate Demand Experiments. An objective of this study, was to develop a technique to estimate the amount of potassium permanganate needed to re-oxidize a media after its adsorption of a known quantity of soluble manganese.

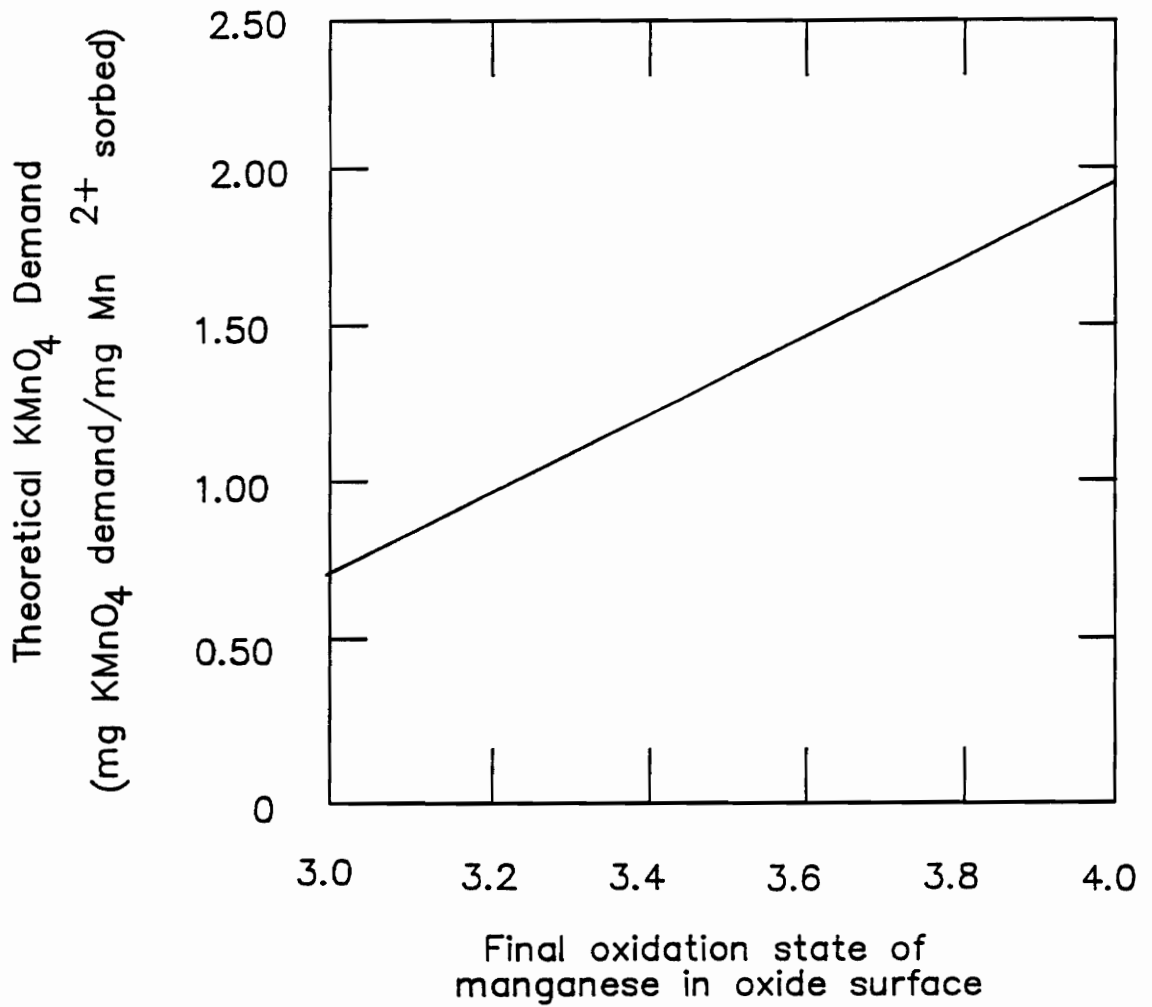


Figure 13. Variation in amount of KMnO_4 required to oxidize Mn^{2+} to $\text{MnO}_x(\text{s})$ as a function of valence state of manganese in the oxide solid phase.

However, the experiments, showed no apparent trend in the data.

Although the results of this study were inconclusive, other applicable data about the adsorptive capabilities of a particular media can be derived through the use of a potassium permanganate demand test. By coupling this type of titration with an HAS extraction of the media surface, the current oxidative state of the surface can be assessed. An abundance of surface extractable manganese but little evidence of surface permanganate demand would indicate that the media coating was well-oxidized. In contrast, an elevated permanganate demand with respect to the amount of surface extractable manganese present adsorbed Mn^{2+} requiring oxidation. This test result indicates that media is near its maximum capacity for Mn^{2+} removal and is relatively ineffective for further soluble manganese uptake.

The Effect of pH and Presence or Absence of Free Chlorine on Rate of Mn^{2+} Uptake by Oxide-Coated Filter Media.

The rate of Mn^{2+} uptake by oxide-coated filter media can be described by the first-order term which was shown earlier in the Methods and Materials section (Equation 12). This has vast implications because it means, regardless of influent manganese concentration, the uptake rate should remain fairly constant for a particular media at a given pH level and free chlorine concentration.

Data presented in Figures 10 and 11 showed the effect of pH on the Mn^{2+} uptake rate constant. The data indicated that as the solution pH increases, the kinetic uptake rate constant also increases. A possible explanation for this may lie in a change in the charge of the oxide surface as a result of pH change. Morgan (3) showed that a zero point of charge is encountered for the oxide surface at a pH around 2.8; further, as the solution pH increases, the charge on the oxide surface becomes increasingly more negative (Figure 14). Therefore, as the surface becomes more negatively charged, there are more potential sites (per unit weight of surface $\text{MnO}_x(\text{s})$ coating) for Mn^{2+} uptake.

The hypothesis then is that the specific concentration of Mn^{2+} adsorption sites has a significant role in defining Mn^{2+} adsorption rates. One way to test this hypothesis would be to operate two filter columns side by side, with differing media. They would be arranged so that a media with a small amount of oxide surface would operate at a high pH condition, while a second media with a larger amount of oxide surface would operate at a lower pH condition. The goal would be to choose operation conditions of Mn^{2+} adsorption which yielded essentially the same specific concentration sites in both columns. If the results of the experiment indicated the same kinetic uptake rates, it would suggest that the number of surface sites was indeed a critical parameter for defining Mn uptake rates.

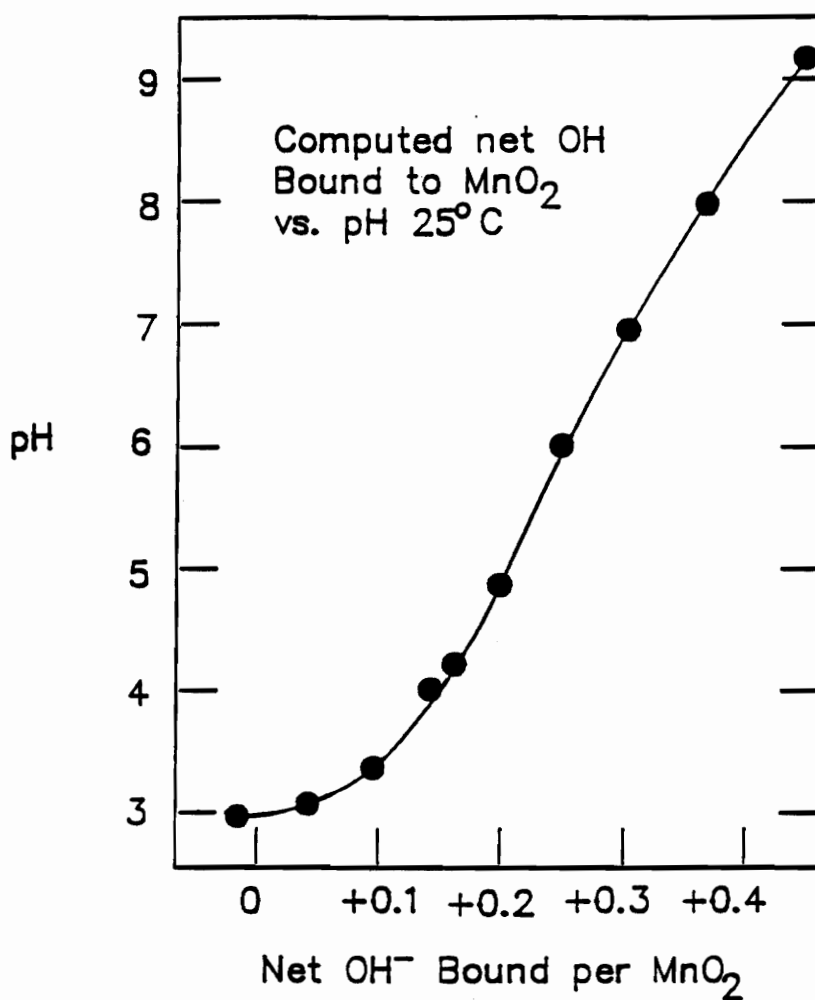


Figure 14. Effect of pH on surface charge of oxide surface. (After Morgan et al.(3)).

Effect of Free Chlorine on Uptake Rates. Free chlorine was added to the solution to determine the impacts that this oxidant might have on the kinetic uptake rate constant. The results of the experiment showed that an increase in the applied free chlorine dose effected a significant increase in the corresponding k-value (Figure 12).

The role of chlorine in the rate of Mn^{2+} uptake may be the oxidation of adsorbed manganese, which would serve to keep the maximum number of surface sites available for adsorption. The enhanced adsorptive capability would cause the concentration of Mn^{2+} near the media surface to be lower compared to that of the bulk solution. The resultant gradient established would draw Mn^{2+} towards the media surface, enhancing the overall rate of removal.

Impact of Oxide Coatings on the Physical Properties of Filter Media

A study was conducted to determine the effects of oxide coatings on the physical properties of the filter media. As summarized in Table 4 of the Results section of this report, no significant impact on the physical size and density properties of the media was observed. These results suggest that the presence of oxide coatings should have little impact on the behavior of filters during filtration or backwash.

Since the specific gravity of manganese oxides range from 4.8 to 5.2 (12), compared to 1.5 for anthracite coal, a media with a manganese oxide coating might be expected to have a specific gravity higher than 1.5 due to the presence of the oxide. However, a significant increase in specific gravity was not observed for any of the media listed in Table 4. This results may be explained by the relative masses of oxide and media which are involved. The greater amount of the media present compared to the quantity of the oxide served to deter any effects of the oxide coating on the overall specific gravity of the media.

There are certain practical implications of these results. First, a surface oxide coating of 10-20 mg MnO_2 (s) per gram of anthracite coal should not necessarily cause this media to intermix to a greater extent with the sand following backwash. Also, since the effective size of the media does not change significantly, due to the oxide surface coating, no significant change in the "clean bed" head loss of the filter would be expected. This lack of growth of media size is important since such growth would potentially cause the depth of the filter to increase, thereby increasing the clean bed head loss and decreasing the available depth for the water column on top of the filter.

In summary, even though certain filter media samples examined in this study exhibited substantial oxide surfaces, these surfaces were found to have minimal impact on both

media size and density. This in turn means that these oxide surfaces have no detrimental impact on the physical characteristics of filtration.

Results Obtained from a Long-term Manganese Adsorption Capacity Study

Thus far, all of the results presented have been from experimental columns in which the media depth was between one and four inches. To help correlate these results with actual water treatment plant filter media depths, an experiment was constructed which employed a total media depth of 23 inches. Sampling ports were placed after each 5-3/4 inches of media depth, so the manganese wavefront could be monitored as it progressed down the depth of the column. The experiment was conducted at a surface loading rate of 3.0 gpm/ft², an influent pH of 7.0, and an influent manganese concentration of 0.50 mg/L.

Data in Figure 15 show the progression of the manganese concentration wavefront through the column. Manganese concentrations observed at 2 hours, 12 hours, 24 hours, and 33 hours after filter start-up are shown by the corresponding line on the figure. In this manner, it is possible to follow the gradual increase of manganese concentration through the filter depth over time. It is interesting to note that even after 24 hours of operation, the filter had not failed with respect to the secondary

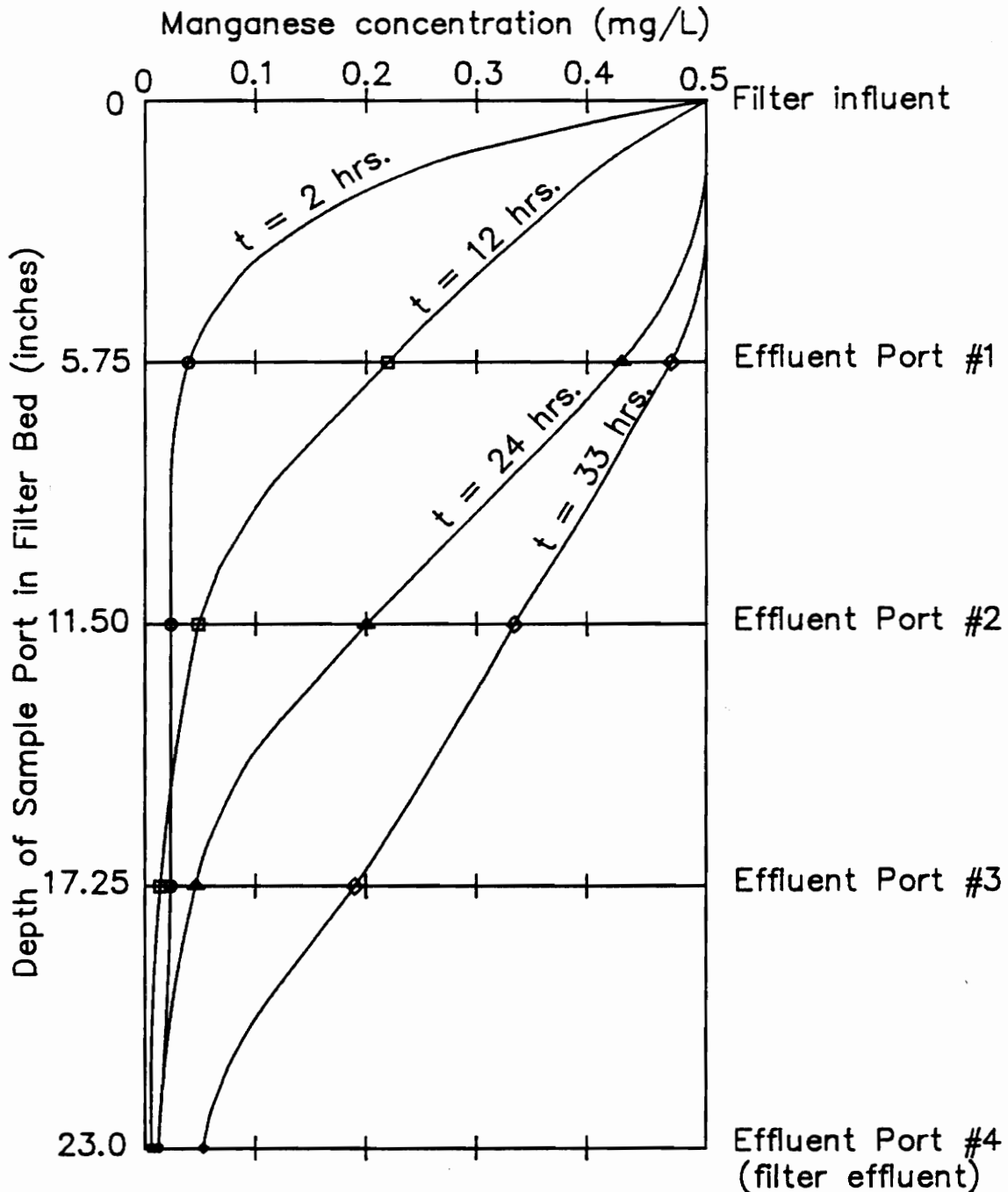


Figure 15. Progression of manganese concentration "wavefront" through the depth of a 23-inch filter column packed with media #1. (pH = 7.0, influent manganese concentration = 0.50 mg/L, filter surface loading rate = 3.0 gpd/ft², amount of manganese on surface of media = 3.90 mg Mn/g of media).

standard for manganese. Only after 33 hours did the filter effluent begin to exceed the secondary standard for manganese. This is a significant length of time, considering that the influent manganese concentration was fairly high (0.50 mg/L) and that the surface oxide coating of the filter media was low (3.90 mg Mn/g of media).

Filter Data Taken from an Actual Water Treatment Plant

In an attempt to correlate the results of this study with what actually occurs in water treatment plants, data was obtained from the Williams Water Treatment Plant, located in Durham, North Carolina. The media used in this plant's filters is an anthracite media which has a surface manganese oxide coating of 40-60 mg manganese/g of media. The water treatment plant typically operates with between 2 and 4 mg/L free chlorine (HOCl) in the filter applied water and at a pH near 6.0 - 6.5.

Data regarding influent soluble and total manganese concentrations through out the water treatment plant are presented in Table 5. Of particular interest, is the manganese concentration data shown as a function of depth location within the filters. The data indicate that most of the soluble manganese that reaches the filters is adsorbed in the top 6-12 inches of media. These results reinforce what the previous results of this study have shown, namely that considerable sorption of soluble manganese occurs in

Table 5
Summary of Manganese Concentrations
Found Throughout the
Williams Water Treatment Facility
Located in Durham, North Carolina

Manganese Concentration (mg/L)																
Date	Raw Water		Settled Water		Filter Applied		Filter Bed Depth								Filter Effluent	
	Total	Soluble	Total	Soluble	Total	Soluble	6"		12"		18"		24"		Total	Soluble
							Total	Soluble	Total	Soluble	Total	Soluble	Total	Soluble		
10/27/87	0.31	0.18	0.20	0.18	0.28	0.31	0.120	0.013	-	-	0.010	0.007	0.003	0.006	0.002	0.008
11/3/87	0.22	0.16	0.22	0.21	0.22	0.20	0.005	0.018	-	-	0.002	0.003	<0.001	0.002	0.003	0.005
11/10/87	0.28	0.14	0.21	0.19	0.20	0.18	0.042	0.005	-	-	0.006	0.015	<0.005	<0.005	<0.005	0.005
11/17/87	0.21	0.15	0.26	0.26	0.23	0.16	0.005	<0.005	-	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
12/2/87	0.38	0.28	0.36	0.34	0.35	0.33	0.23	0.22	0.04	0.048	0.017	0.005	<0.005	<0.005	<0.005	<0.005
12/9/87	0.38	0.30	0.38	0.35	0.38	0.36	0.24	0.22	0.05	0.05	0.026	<0.005	<0.005	<0.005	<0.005	<0.005
01/27/88		0.29	0.38	0.37	0.38	0.37	0.37	0.34	0.06	0.04	0.03	0.02	0.01	0.004	0.03	0.008

oxide coated filters and that this process is typically a rapid one.

The Durham Water Treatment Plant does chlorinate prior to filtration, and the free chlorine aids in the efficiency of manganese removal through the filters. The addition of free chlorine as mentioned earlier, seems to help maintain a continuously oxidized surface on the oxide coating. In this manner, the filters exhaust their manganese sorption capacity at a very slow rate. It should be noted that the Williams Water Treatment Plant has successfully removed Mn^{2+} via the combined use of pre-filter chlorine addition and adsorption/oxidation on the oxide-coated filter media for over a decade.

Prediction of Soluble Manganese Breakthrough through a Water Treatment Plant Filter

An attempt was made to correlate the results of the capacity experiments with the results of the kinetic experiments in order to obtain an expression which would allow one to predict when a particular concentration of soluble manganese would break through the effluent side of a oxide-coated filter.

Figure 16 shows the conceptual orientation of a theoretical Mn^{2+} concentration wavefront curve. An attempt was made to determine a way to estimate the wavefront depth, d_w . Recalling first-order decay expression (Equation 12),

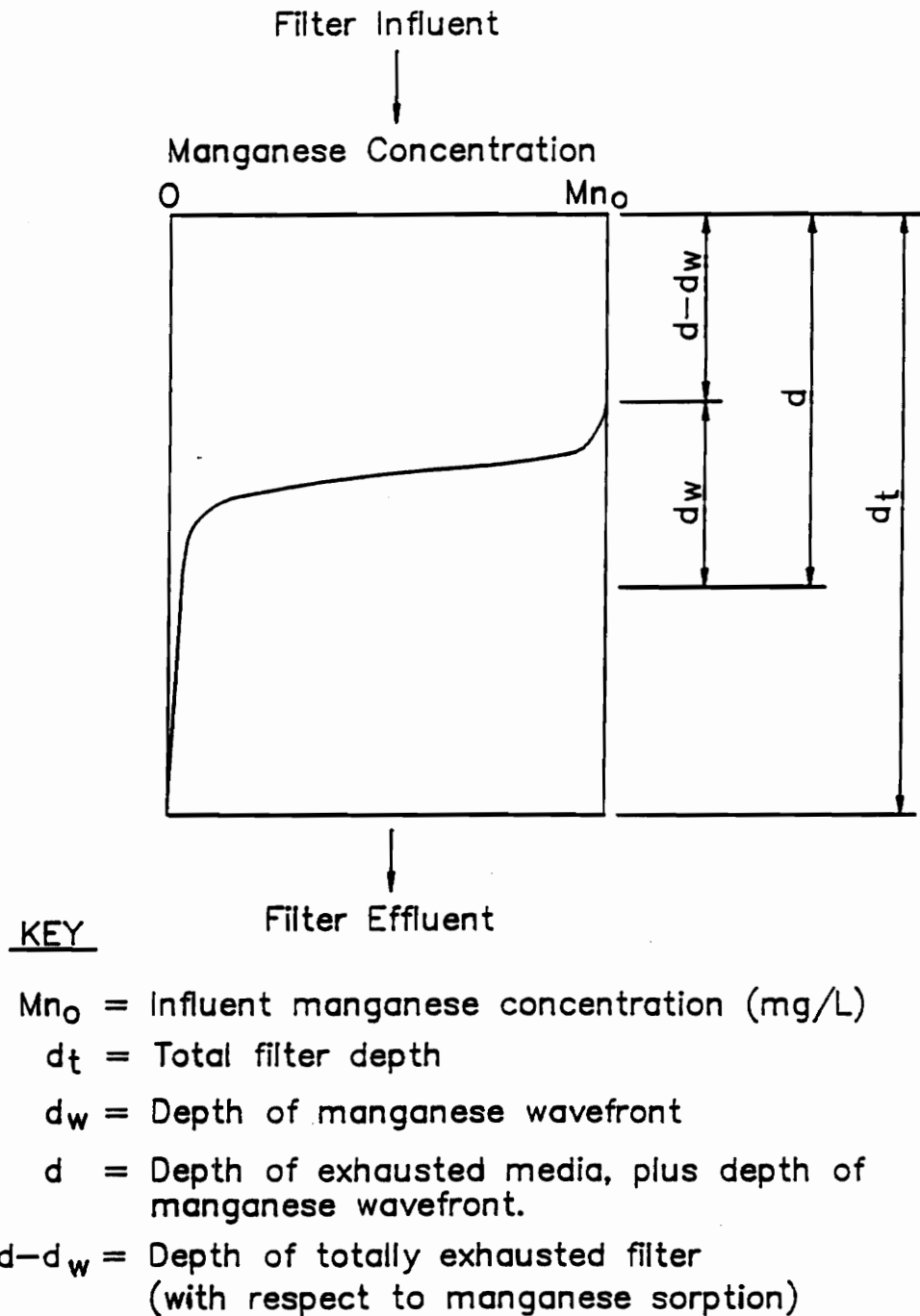


Figure 16. Schematic showing the orientation of the theoretical manganese concentration wavefront which was used in the formulation of the manganese breakthrough model.

hydraulic residence time may be replaced by the following expression:

$$t = \frac{d_w(\epsilon)(7.48)}{L.R.} \quad [18]$$

where:

d_w = depth of wavefront, feet
 $L.R.$ = loading rate, gpm/ft²
 ϵ = filter bed porosity

All other terms are the same as defined in equation 12.

Replacing t in Equation 12 yields:

$$Mn_t = Mn_0 e^{\left(\frac{-k(7.48(\epsilon)(d_w))}{L.R.} \right)} \quad [19]$$

Equation 19 represents the basis for Figures 17, 18, and 19. A value of 0.025 mg/L was arbitrarily selected for the effluent manganese concentration (Mn_t) for all cases. This value is one half of the current standard for manganese and, thus, should be conservative enough for design applications. The k -values used in equation 19 were selected from Figures 10, 11, and 12 for appropriate operating conditions. In order to normalize the plots, a loading rate of 1 gpm/ft² was assumed. Therefore, one figure could theoretically be used for any loading rate, given all other conditions were constant. Figure 17 and 18 were derived purely on a kinetics basis. Results presented both figures clearly

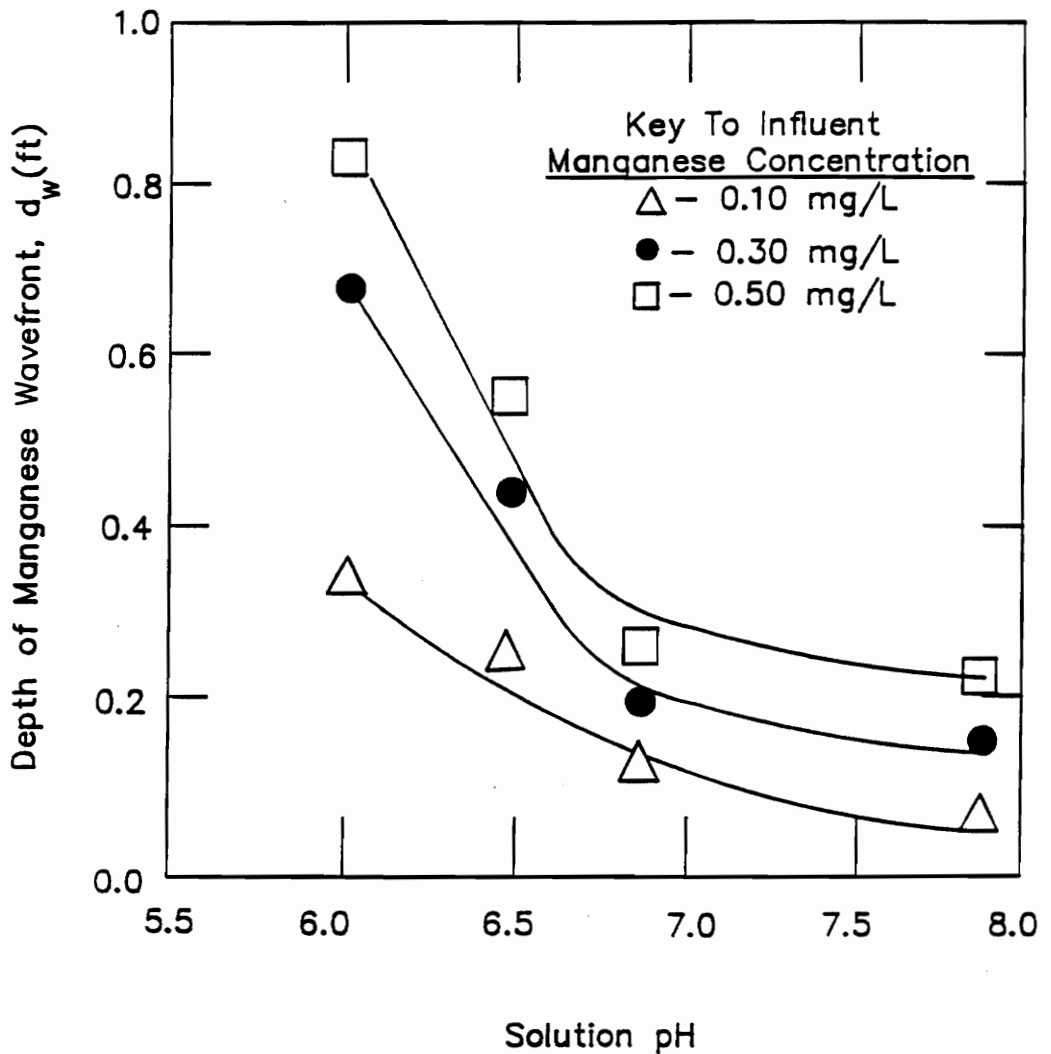


Figure 17. Effect of pH on the depth of manganese wavefront for media #7 at different influent manganese concentrations. (Effluent manganese concentration = 0.025mg/L, filter surface loading rate = 1.0gpm/ft² amount of manganese on the surface of the media = 1.65 mg Mn/g media; no HOCl).

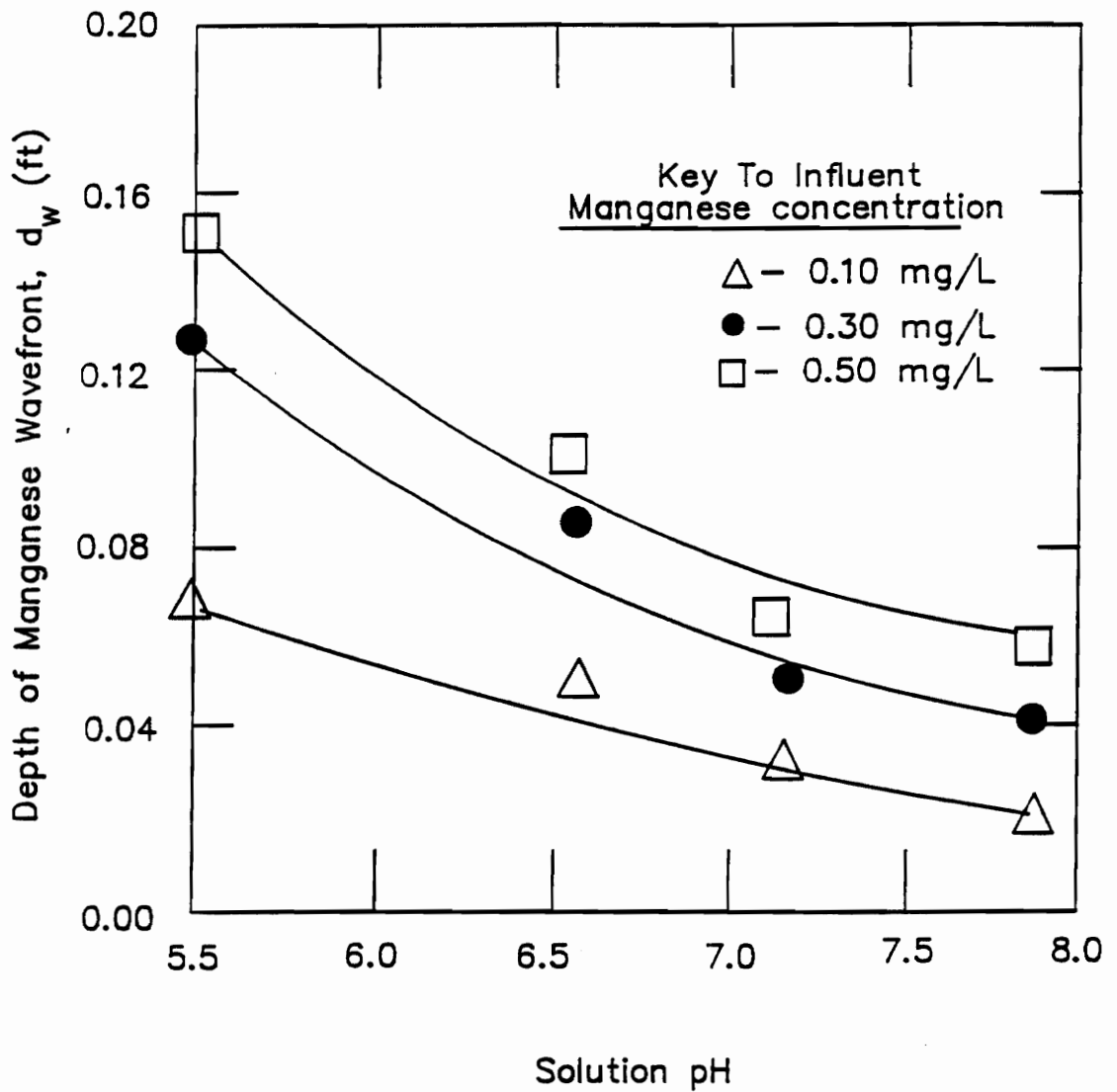


Figure 18. Effect of pH on the depth of manganese wavefront for media #1 at different influent manganese concentrations. (Effluent manganese concentration = 0.025 mg/L, filter surface loading rate = 1.0 gpm/ft², amount of manganese on the surface of the media = 3.90 mg Mn/g media; no HOCl).

illustrate what can be inferred in the kinetics section; that as pH increases, the depth of the wavefront decreases. In other words, as the solution pH increases, the efficiency of manganese sorption on the surface of the media improves.

Figure 19 is a plot similar to Figures 17 and 18; however, chlorine has been added to solution in Figure 19. As the chlorine concentration increases, the manganese removal efficiency also increases (as shown by the decrease in wavefront depth).

By using Figure 16, a formula can be derived for calculating time to breakthrough at a certain effluent concentration in a filter. The procedure is as follows: Given a known surface coating of manganese oxide on a filter media, a family of curves can be generated like those represented in Figures 17 and 18. Given a known solution pH and a known influent manganese concentration, a "manganese wavefront depth", (d_w) can be determined from the appropriate graph. By using the following equations in conjunction with manganese sorption capacity data and kinetic uptake rate data, an estimate of time to breakthrough can be made.

$$M = 455 \cdot UR \cdot (d - d_w) \cdot A \cdot p_m \cdot \epsilon \cdot (s.m.) \quad [20]$$

$$r = 5450 \cdot C_{in} \cdot A \cdot L.R. \quad [21]$$

$$t_b = M/r \quad [22]$$

where:

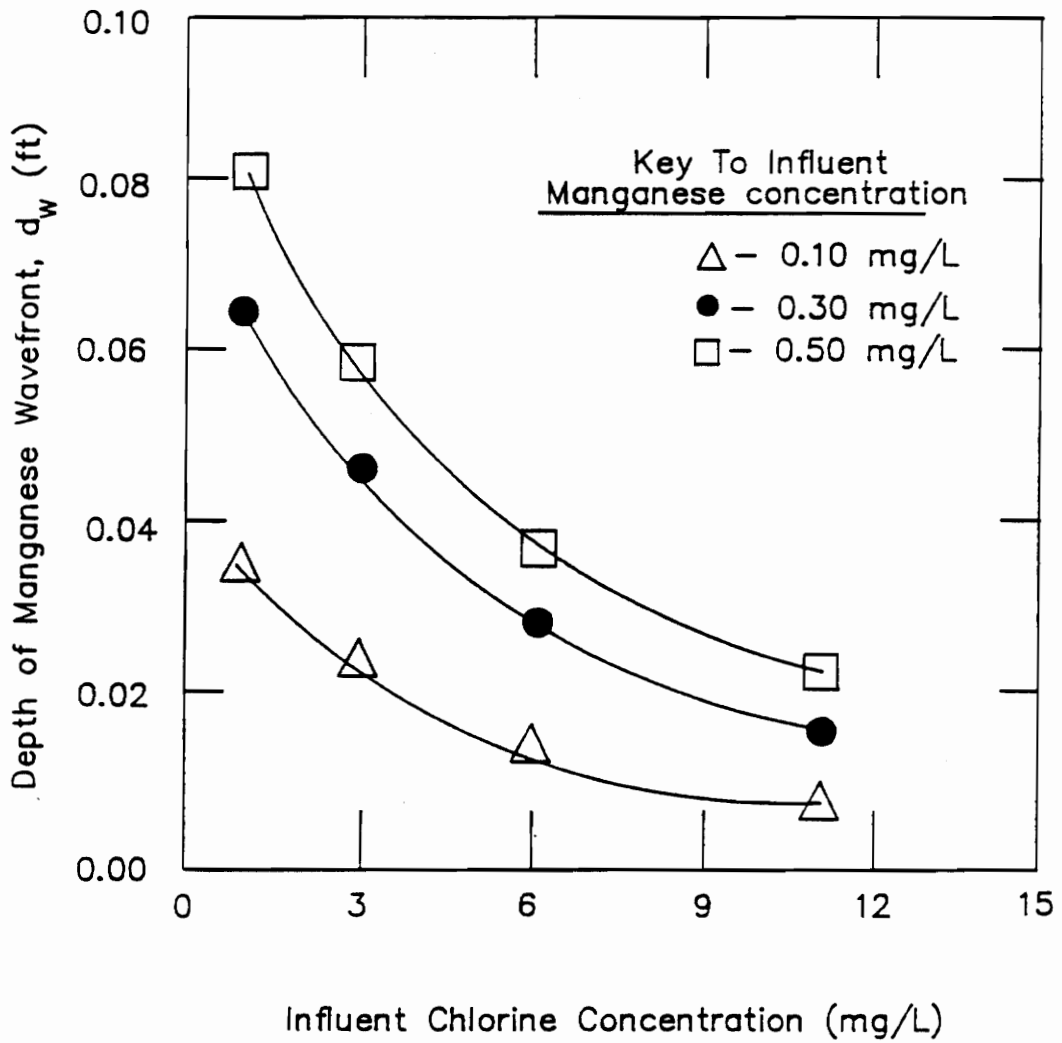


Figure 19. Effect of influent chlorine concentration on the depth of manganese wavefront for media #1 at different influent manganese concentrations. (Effluent manganese concentration = 0.025mg/L, filter surface loading rate = 1.0 gpm/ft², pH = 7.1, amount of manganese on the surface of the media = 3.90 mg Mn/g media).

- M = amount of manganese sorbed by the filter, mg
 UR = uptake ratio, or the amount of soluble manganese the media can sorb per amount of media, (mg Mn sorbed/mg Mn on surface of media).
 d = total depth of filter media, ft
 d_w = depth of wavefront, ft
 A = surface area of filter, ft^2
 p_m = density of media, lb/ft^3
 ϵ = porosity
 $s.m.$ = surface manganese content of the filter media, mg Mn/g media.
 C_{in} = influent manganese concentration, (mg/L)
 $L.R.$ = liquid loading rate, (gpm/ ft^2)
 t_b = time to breakthrough
 M = amount of manganese sorbed by the filter media
 r = rate of manganese uptake (mg/day)

Example Manganese Breakthrough Calculation

The following is an example of how the model could be used to estimate the "life expectancy" of a filter without any reoxidation of the surface of the media. Typical values for the various parameters have been used; a media with a 3.90 mg of manganese/g media surface coating was selected since design plots were generated in this study for this type of media. Also, it was assumed that the filter influent contains no free chlorine.

Assumed Values for Parameters:

Filter loading rate, L.R.	= 4 gpm/ft ²
Surface manganese coating, s.m.	= 3.90 mg Mn/g media
Filter applied water pH	= 7.0
Filter depth	= 24 inches
Filter area	= 300 ft ²
Influent manganese concentration	= 0.30 mg/L
Porosity of media	= 0.42
Media Density	= 93.6 lb/ft ³

Various figures developed in this study were used in the calculation of the estimated time for manganese breakthrough. A brief description of the methodology follows:

From Figure 8, the manganese sorption capacity, m.s., at pH=7 is 0.35 mole of Mn^{2+} /mole of $MnO_x(s)$. At a pH of 7.0 and an influent manganese concentration of 0.3 mg/L, the depth of wavefront, d_w , for the media in question is 0.065 ft (from Figure 18). This, however, is the depth of wavefront for a filter surface loading rate of 1 gpm/ft². In order to obtain the depth of wavefront for this particular case, the d_w term must be multiplied by the actual surface loading rate of 4.0. Therefore, the term d_w is equal to 0.23 ft. The mass of manganese, M, which the filter has sorbed when the effluent reaches 0.025 mg/L is 12.7×10^6 mg. The mass loading rate of manganese on the filter, r, is 2.0×10^6 mg/day from Equation 21. By using Equation 22, the time at which the effluent of the filter reaches a concentration of 0.025 mg/L of Mn is 6.4 days.

The results of this example suggest that, in the fully oxidized state, a filter with a reasonable surface oxide coating ($>3-4$ mg Mn/g media) can withstand fairly high loadings of manganese (0.3 mg/L in this case) without exceeding effluent limitations for manganese. This implies that filters can function reasonable well as a site for manganese removal. However, a well oxidized media surface would have to be present in order for this method to be reliable. Without a well oxidized surface, the media surface could exhaust its ability to sorb manganese, leaving no "buffer zone" for manganese removal between the water treatment plant and the distribution system.

Practical Applications from the Manganese Sorption Capacity and Uptake Kinetics Studies

These studies showed that both chlorine and pH have a big impact on manganese uptake rate kinetics. Also, pH has a great impact on the manganese adsorption capacity of the oxide surface. These studies suggest that a water treatment plant filter that has a reasonable amount of manganese oxide coating (>2 mg manganese/g of media) can function well in the sorption of soluble manganese.

Recent studies made by Occiano (13) have revealed that the presence of chlorine in the filter applied water results in the continual regeneration of the oxide surface, thus

allowing such filters to operate in the continuous fashion without exhausting the surface uptake capacity. Therefore, plants that minimize or eliminate free chlorine from in front of their filters may drastically reduce their Mn^{2+} uptake rate, possibly leading to breakthrough of manganese into the filter effluent. Also, the reduction of filter applied water pH (as part of, for example, an effort to get better removal of organics by coagulation) would also reduce the rate of uptake.

CONCLUSIONS

The primary goals of this study were to characterize the manganese sorption capacity and uptake rate kinetics of oxide-coated water treatment plant filter media. Laboratory studies were performed to obtain both sorption capacity data and kinetic data. The data obtained during the manganese sorption capacity study seemed to correlate reasonably well with the results of Morgan and Stumm (3).

The significant conclusions that can be drawn from this research are:

1. Manganese sorption on oxide-coated media is pH-dependent. Specific manganese uptake (based on manganese sorption per unit mass of filter media) is independent of surface manganese concentration.
2. The uptake rate kinetics of manganese sorption on oxide-coated media appears to be of the first order. The sorption rate is dependent on pH. The addition of free chlorine can substantially increase the rate of manganese adsorption.
3. The physical characteristics of filter media are not affected by the presence of an oxide coating. Neither size nor density of the media increased noticeably as a result of the presence of an oxide coating, even when the surface coating was as much as 60 mg of manganese per gram of media.

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VITA

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