To the Graduate Council

I am submitting herewith a thesis written by Brett W. Frazier entitled "Field Studies in Iron and Manganese Sequestration." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the Master of Science, with a major in Environmental Engineering.

R. Bruce Robinson, Major Professor

We read this thesis and
recommend its acceptance:

Accepted for the Council:

Vice Provost
and Dean of The Graduate School

FIELD STUDIES IN IRON AND MANGANESE SEQUESTRATION

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Brett W. Frazier

December 1988

DEDICATION

This thesis is dedicated to my parents Jimmy F. Frazier and Lyndal D. Frazier who, at much sacrifice, gave financial and personal support for my education when most needed.

ACKNOWLEDGMENTS

I wish to express my gratitude to Doctor Bruce Robinson for his support and guidance toward my research. Also, gratitude goes to Doctors Gregory Reed and Dennis Weeter for serving on my committee and for critically examining my thesis. I also give special thanks to Venkatesh Chidambariah, Danny Christodos, Willard Harms, and Kevin Klueh for their invaluable assistance in the laboratory. I also wish to acknowledge the town of Rainelle, West Virginia, the villages of Butler and Waukesha, Wisconsin, and the communities of Aurora and Oak Ridges, Ontario, Canada for their cooperation and assistance during the field tests. Appreciation is forwarded to the American Waterworks Association Research Foundation for funding of the research and to the PQ Corporation of Valley Forge, Pennsylvania for providing *gratis* the sodium silicate solutions used in this research. Finally, I wish to thank Professor Bernard Fredrick and Doctor John Snider for granting graduate assistantships during the final stages of the research.

ABSTRACT

Operating characteristics in iron and manganese sequestration are poorly understood. Most of the knowledge is laboratory based and needs to be expanded to the field. The primary objective of this study is to (1) develop detailed, quantitative documentation of effectiveness of sequestering in actual systems, (2) compare previous results and conclusions reported in the literature review with field findings, and (3) optimize the sodium silicate-chlorine method for iron control in the presence of calcium. Secondary objectives are to determine the effects on sequestering by water heaters and by neutral pH.

Data were collected both from the laboratory and the field. Laboratory results were obtained by treating a deaerated model groundwater containing 2 ppm of ferrous iron with sodium silicate and sodium hypochlorite. Tests were run over a five day period recording the filterable iron, total iron, turbidity, and pH for the various dosages involved. Field results were obtained by collecting samples at various points at each location and recording the data after the samples were brought back to the lab.

Both field and laboratory results show that stabilization is only temporal, that calcium reduces the length of stabilization, that an increase in the silica dosage increases the length of treatment in the presence of calcium, that long lag times between the silicate and chlorine dosages are not efficient to treatment, that stabilization breaks down faster at elevated temperatures, that no treatment is more favorable in manganese stabilization, and that objective, scientific field studies are able to characterize and quantify the success of sequestration at field sites. Other conclusions are that 0.45 μm filter results correlated slightly better with actual field practices than the 0.1 μm filter results, that better treatment at high pH are conflicting with previous studies where low pH was more favorable, and that previous results of laboratory studies have been shown to closely model field conditions.

TABLE OF CONTENTS

SECTION PAGE

I. INTRODUCTION 1

II. LITERATURE REVIEW 4

Aqueous Iron And Manganese Chemistry 4

Ferrous Iron and Manganese Oxidation 4

Iron and Manganese Precipitates 6

Iron and Manganese Solubility 7

Aqueous Silicate Chemistry 12

Silicate Solubility 12

Commercial Sodium Silicate Solutions 15

Interaction Of Silica, Iron, Manganese, And Other Metal Ions 16

Iron and Manganese Sequestration 20

Iron Field Studies 20

Iron Laboratory Studies 28

Manganese Field Studies 32

Manganese Laboratory Studies 35

III. METHODS AND MATERIALS 37

Sequestration Of Model Iron Containing Groundwater 37

Optimization In The Presence Of Calcium Ions 40

Field Procedures 40

IV. RESULTS 42

Optimization In The Presence Of Calcium 42

Practice Field Test At Ranielle, W. Va 53

Wisconsin Field Studies 63

Case History of Waukesha [43] 63

Results of Waukesha Field Study 67
Case History of Butler [45] 72
Results of Butler Field Study 74
Ontario, Canada Field Studies 77
Case history of Oak Ridges [46] 77
Sampling Procedures at Oak Ridges 81
Results of Oak Ridges Field Study 83
Case History of Aurora [46] 91
Sampling Procedure at Aurora 91
Results of Aurora Field Study 94
V. DISCUSSION OF RESULTS 102
VI. CONCLUSION 106
VII. RECOMMENDATIONS FOR FURTHER STUDIES 108
BIBLIOGRAPHY 110
APPENDIX 115
VITA 118

LIST OF TABLES

TABLE PAGE

1. Characteristics of Waters That Were Successfully Treated by Dart and Foley..... 22
2. Five-day results of test 1 in which approximately 2 ppm iron was dosed with 12.3-13.6 ppm as SiO2..... 43
3. Five-day results of test 2 in which approximately 2 ppm iron was dosed with 25.4-28.0 ppm as SiO2..... 47
4. Five-day results of test 3 in which approximately 2 ppm iron was dosed with 20.1-21.0 ppm as SiO2..... 50
5. Five-day results of test 4 in which approximately 2 ppm iron was treated in the presence of 155-157 ppm as $CaCO_3$..... 54
6. Five-day results from Ranielle iron stabilization field test in the presence of calcium and manganese..... 58
7. Five-day results from Waukesha iron stabilization field test in the presence of calcium and magnesium. 68
8. Five-day results from Butler iron stabilization field test in the presence of calcium and magnesium 75
9. Five-day results from Oak Ridges iron stabilization field test in the presence of calcium and magnesium. 84
10. Filterability through a 0.45 μm filter. 84
11. Five-day results from Aurora iron stabilization field test in the presence of calcium and magnesium. 95
12. Filterability through a 0.45 μm filter. 95

LIST OF FIGURES

FIGURE PAGE

1. Ferric iron solubility diagram. 9
2. Ferrous iron solubility diagram. 9
3. Manganese (II) solubility diagram. 11
4. Silicate solubility diagram. 14
5. Filterable iron of samples from Test 1. 44
6. Turbidity of samples from Test 1. 44
7. pH of samples from Test 1. 45
8. Total iron concentrations of samples from Test 1. 45
9. Filterable iron of samples from Test 2. 48
10. Turbidity of samples from Test 2. 48
11. pH of samples from Test 2. 49
12. Total iron concentrations of samples from Test 2. 49
13. pH of samples from Test 3. 51
14. Filterable iron of samples from Test 3. 51
15. Turbidity of samples from Test 3. 52
16. Total iron concentrations of samples from Test 3. 52
17. Filterable iron of samples from Test 4. 55
18. Turbidity of samples from Test 4. 55
19. Total iron concentration of samples from Test 4. 56
20. pH of samples from Test 4. 56
21. 1985 Ranielle Water Analysis Report Source 57
22. Filterable iron samples from Ranielle, W. Va. 60
23. Turbidity of samples from Ranielle, W. Va. 60
24. pH of samples from Ranielle, W. Va. 61

25. Total iron concentrations of samples from Ranielle, W. Va. 61
26. Apparent color of samples from Ranielle W. Va. 62
27. Filterable manganese from Ranielle, W. Va. 62
28. Total manganese concentrations of samples from Ranielle, W.Va. 63
29. Waukesh well data 64
30. Diagram of typical sodium silicate application at Waukesha. 66
31. Raw water analysis at Wolf Rd Well #10 69
32. Filterable Iron samples from Waukesha, Wisc. 69
33. pH of samples from Waukesha, Wisc 71
34. Turbidity of samples from Wauksha, Wisc 71
35. Apparent color of samples from Wauksha, Wisc. 72
36. Filterable iron samples from Butler, Wisc. 76
37. Total iron concentrations of samples from Butler, Wisc. 76
38. Turbidity of samples from Butler, Wisc. 78
39. pH of samples from Butler, Wisc 78
40. Apparent color of samples from Butler, Wisc. 79
41. Water quality of Oak Ridges conducted by the Ministry of Environment (M.O.E.) as of July 30, 1987 80
42. Monthly flow and consumption of chlorine and sodium silicate, and average flow of each well at Oak Ridges. 82
43. Filterable iron through a 0.1 μm filter from Oak Ridges, Ontario. 85
44. Apparent color of samples from Oak Ridges, Ontario 86
45. Turbidity of samples from Oak Ridges, Ontario. 86
46. pH of samples from Oak Ridges, Ontario. 87
47. Total iron concentration of samples from Oak Ridges, Ontario. 88
48. Filterable iron through a 0.45 μm filter at Oak Ridges, Ontario 88
49. Filterable manganese through a 0.1 μm filter from Oak Ridges 89

50. Filterable manganese through a 0.45 μm filter from Oak Ridges. 90
51. Total manganese concentration of samples from Oak Ridges. 90
52. Raw water analysis of Aurora by M.O.E. as of October 5, 1987 92
53. Total monthly flows and average flows for each well in Aurora for 1987 93
54. Filterable iron through a 0.1μm filter from Aurora, Ontario 96
55. Turbidity of samples from Aurora, Ontario 96
56. Apparent color of samples from Aurora, Ontario. 97
57. Total iron concentration of samples from Aurora, Ontario 97
58. pH of samples from Aurora, Ontario 99
59. Filterable iron through a 0.45 μm filter from Aurora, Ontario. 99
60. Filterable manganese through a 0.1 μm filter from Aurora. 100
61. Filterable manganese through a 0.45 μm filter from Aurora 100
62. Total manganese concentration of samples from Aurora, Ontario. 101

I. INTRODUCTION

Groundwater is a common source for small community water supplies. It typically contains many dissolved minerals which reflects the geology of the aquifer [1]. Some of these dissolved inorganic materials, especially hardness-causing divalent ions, such as calcium and magnesium, and reduced iron and manganese ions, must be removed or reduced in concentration before industrial or domestic consumption [2].

Iron and manganese both exist primarily in the reduced divalent state in groundwater, which, under unaerated conditions, is not a problem. But when this water is aerated, iron and manganese will be oxidized to iron (III) and manganese (III) or (IV), respectively. In their oxidized state, iron and manganese create an aesthetic problem of red water, which leads to the staining of laundry and plumbing fixtures by the oxidized precipitates.

The secondary standards for iron is 0.3 ppm and for manganese is 0.05 ppm [3]. Above these concentrations iron and manganese will precipitate out of solution upon oxidation. In many midwestern states, approximately 50% of the public water supplies exceed the secondary drinking water standards for iron [4] and from a 21 state survey, 35% of the systems exceed the iron secondary standard and 20% exceed the manganese secondary standard [5]. In Tennessee the average iron concentration is greater than 0.3 ppm for all of the major aquifers but one [6].

Conventional treatment for excess iron and manganese laden groundwater is an aeration and filtration process. Iron and manganese are oxidized by aeration and/or chemically oxidized by a stronger oxidant. In the oxidized state, the metals form precipitates which are then filtered from the water. Under proper supervision this treatment

is very efficient for iron and manganese removal, but the costs of construction, operation, and maintenance can be taxing on a small community.

A less expensive alternative is chemical sequestration, which prevents the oxidized iron and manganese from causing objectable turbidity and color without the removal of the metals from the water. Polyphosphate and sodium silicate solutions are the main sequestering chemicals. In the past, polyphosphate solutions have been mass-marketed as the better sequesterent over sodium silicate solutions, but no studies have been published which determine which is the better sequesterent. Tests conducted at The University of Tennessee under the American Water Works Association Research Foundation funding have shown that in the absence of high hardness iron can be successfully sequestered with polyphosphate and sodium hypochlorite [7], and that manganese can be sequestered by polyphosphate [8]. Tests are pending at UT to compare the effectiveness and cost of polyphosphates to sodium silicate. For the remainder of this thesis only sodium silicate will be considered as the sequesterent in question.

Sodium silicate has been used successfully as a sequesterent for iron control by the Ontario, Canada Ministry of the Environment as early as 1969 [9], and has also been tested by them for the sequestering of manganese [10]. Iron can be sequestered by the simultaneous or near simultaneous injection of sodium silicate and sodium hypochlorite (or chlorine gas) into the groundwater at the well head. As a result, water with low turbidity and color can be distributed into the system.

Laboratory studies have shown that calcium,most likely magnesium, and, to a lesser extent, sodium [4], have an adverse effect on the control of iron and manganese. When calcium is present the period of sequestration is reduced.

The basics of sodium silicate sequestration are not fully understood. This study was not designed to deduce the basics of sequestration, but rather it was designed to develop a better understanding of the operating characteristics in field treatment. Most of the knowledge of sequestration is laboratory based and needs to be expanded to field

practices. Field research was needed to determine if the laboratory findings were corresponding to field conditions.

The primary objective of this thesis is to evaluate results from laboratory tests in field conditions. Scientific field observations regulated by laboratory procedures are needed as a comparison to results obtained in the laboratory. The primary objective includes the following (1) to develop detailed, quantitative documentation of effectiveness of sequestering in actual systems, (2) to compare previous results and conclusions reported in the literature review with field findings, and (3) to optimize the sodium silicate-chlorine method for iron control in the presence of calcium. Comparisons of the data will indicate whether or not laboratory results are correlating with actual field conditions. Secondary objectives of the study was to determine the effects on sequestering by high temperature water heaters and by neutral pH.

II. LITERATURE REVIEW

A background of iron, manganese, and silica chemistry is provided in this review with the information pertaining mainly to the subject of the thesis. Iron and manganese will be discussed separately from silica and then together as the three interact in the sodium silicate sequestration method.

Aqueous Iron And Manganese Chemistry

Ferrous Iron and Manganese Oxidation

Iron and manganese commonly exist in their reduced form in groundwater and will, depending upon pH, oxidize upon exposure to oxygen. The rate of iron and manganese oxidation is pH dependent. Below pH 6.0, the oxidation rate is very slow [2] and below pH 3.0 it is independent of pH [6]. Above pH 5.5 the oxidation rate is dependent upon the square of the hydroxyl concentration as exemplified in equation 1 [11] so that one unit increase in pH will increase the oxidation rate of iron by 100- fold [4]:

$$\frac{-d\,[Fe(II)]}{d\,t} = k\,[Fe(II)]\,[OH^-]^2 p_{O_2} \qquad (1)$$

where $k = 8.0\ (\pm\ 2.5) \times 10^{13}\ min^{-1}atm^{-1}mol^{-2}l$ at 20° C.

A more convenient form [S&M] of the above equation is :

$$\frac{-d\,[Fe(II)]}{d\,t} = \frac{K_H[O2\ (aq)]}{[H^+]^2}\,[Fe(II)] \qquad (2)$$

where $K_H = 3 \times 10^{-12}$ mol/min-l at 20° C.

The oxidation rate is a first order reaction with respect to ferrous iron and oxygen, and a second order reaction with respect to the hydroxyl ion.

Manganese oxidation occurs at a slower rate than that of iron at neutral pH values. Upon aeration, manganese (II) oxidizes to manganese (III) or(IV) and precipitates. Aeration alone is not very efficient for oxidizing manganese. Therefore a stronger oxidant, such as chlorine or potassium permanganate, is needed for expedient oxidation.

Manganese oxidation is an autocatalytic reaction and can be shown in the following equation [S&M]:

$$\frac{-d\,[\mathrm{Mn(II)}]}{d\,t} = k_0\,[\mathrm{Mn(II)}] + k\,[\mathrm{Mn(II)}]\,[\mathrm{MnO_2}] \qquad (3)$$

$$\text{where } k = k'\,[\mathrm{OH^-}]^2\,p_{\mathrm{O_2}}.$$

The reactions may follow these unbalanced equations [11]:

$$\mathrm{Mn(II)} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{MnO_2\,(s)\ (slow)} \qquad (4)$$

$$\mathrm{Mn(II) + MnO_2\,(s) \rightarrow Mn(II) \cdot MnO_2\,(s)\ (fast)} \qquad (5)$$

$$\mathrm{Mn(II) \cdot MnO_2\,(s) + \tfrac{1}{2}O_2 \rightarrow 2\,MnO_2\,(s)\ (slow)} \qquad (6)$$

The autocatalytic nature of this reaction could be significant for manganese oxidation in distribution systems [12].

Chlorine is commonly used as an oxidant in iron and manganese removal processes. Chlorine is thought to be a rapid oxidant of iron [13]. It increases the rate of iron oxidation by providing a pathway for a lower energy of activation [14]. On the other hand, manganese oxidation is very slow by chlorine below pH 8.0 [13]. It is a common misconception that chlorine easily oxidizes manganese. Chlorine dioxide has been found to be a better oxidant over a wider pH range in manganese oxidation [13].

The rate of iron and manganese oxidation can be increased by various catalysts. Ionic concentration of certain elements and organics can effect the rate of iron and manganese oxidation. Trace amounts of copper, cobalt, and silica ions have a catalytic effect upon iron and manganese oxidation [2]. Copper at a concentration of 0.1 ppm can increase the iron oxidation rate by 5-6 times [2]. Stumm and Morgan noted no marked effects of copper upon the oxidation of manganese [11]. Manganese oxides are thought to catalyze manganese oxidation in distribution mains [14]. Some organic complexes of Fe (II) and Mn (II) can retard oxidation and hold the Fe(II) and Mn (II) in solution at higher pH levels [2].

Iron and Manganese Precipitates

Upon oxidation of iron (II) and manganese (II), an iron oxyhydroxide and manganese oxide, or hydroxide, precipitate will form at a neutral or greater pH. A pH of 7.5 or greater is suggested by Viessmann and Hammer for iron oxygenation and a pH of 9.5 or greater for manganese oxygenation [2]. The result of these precipitates is an unaesthetic effect upon the drinking water causing a colored water which stains laundry and plumbing fixtures and causes taste and odor problems.

Work by Robinson [15] identified crystalline lepidocrocite as the iron precipitate upon aeration of a model groundwater at 20-25° C with a neutral pH, an alkalinity of 400-500 mg/l as HCO_3^-, ferrous iron concentration of 10 mg/l, and a silica concentration of 7 mg/l or less. At higher silica dosages, i. e. greater than 7 mg/l as SiO_2, an amorphous ferrihydrite formed.

Schwertman and Taylor [16] looked at the types of ferric precipitates formed under various conditions of pH, temperature, ferrous to ferric ratios, and oxidation rates. Their findings show that lepidocrocite is the prevalent precipitate under conditions of rapid oxidation and a 100% ferrous iron. Maghematite precipitated at a slow oxidation rate, high temperatures, 90% ferrous iron, and pH of 6-7. Ferrihydrite precipitation occurred at high

initial ferric to ferrous ratios. Given the conditions of silica concentrations and high oxidation rates by strong oxidants, such as chlorine, for a groundwater treatment plant, crystalline lepidocrocite and amorphous ferrihydrite are the principal precipitates of aeration, even though pH conditions at a treatment plant suggest the formation maghematite.

Iron and Manganese Solubility

The solubility of lepidocrocite and amorphous ferrihydrite is very important in either iron removal or iron sequestration processes. The engineer needs to know the iron solubility constants in order to either precipitate the iron for removal or keep the iron in solution for sequestration under various pH values and iron concentrations. The solubility equations for these precipitates are expressed for $Fe(OH)_3$ in a $3M$ $NaClO_4$ solution at a temperature of 25° C [11]:

$$(am)\ Fe(OH)_3\ (s) = Fe^{3+} + 3\ OH^- \qquad \log k_{s0} = -38.7 \qquad (7)$$

$$(am)\ Fe(OH)_3\ (s) = FeOH^{2+} + 2\ OH^- \qquad \log k_{s1} = -27.5 \qquad (8)$$

$$(am)\ Fe(OH)_3\ (s) = Fe(OH)_2^{+} + OH^- \qquad \log k_{s2} = -16.6 \qquad (9)$$

$$(am)\ Fe(OH)_3\ (s) + OH^- = Fe(OH)_4^- \qquad \log k_{s4} = -4.5 \qquad (10)$$

These equations can be rearranged to determine the equilibrium concentration at any given pH [4]:

$$[Fe^{3+}] = k_{s0}\left(\frac{[H^+]}{K_w}\right)^3 \qquad (11)$$

$$[Fe(OH)^{2+}] = k_{s1}\left(\frac{[H^+]}{K_w}\right)^2 \qquad (12)$$

$$[Fe(OH)_2^{+}] = k_{s2}\frac{[H^+]}{K_w} \qquad (13)$$

$$[Fe(OH)_4^{-}] = k_{s4}\frac{K_w}{[H^+]} \qquad (14)$$

where $K_w = 10^{-14}$ = the dissociation constant for water at 25° C.

From equations 11-14, a solubility diagram for iron can be drawn by plotting the pH versus the negative log of the equilibrium concentration of the soluble species (figure 1). The solubility line for $Fe(OH)_3$ can be determined by the summation of the ion species' equilibrium concentration at a given pH. Where one specious predominates, its equilibrium line will closely coincide with the solubility boundary. Maximum solubility of (am) $Fe(OH)_3$ (s) occurs at low pH values where Fe^{3+} is the dominant species and minimum solubility occurs at high pH values where $Fe(OH)_4^-$ and $Fe(OH)_2^+$ are the predominant species. At a neutral pH range of 6-8 for groundwater, (am) $Fe(OH)_3$ (s) is virtually insoluble and the predominant species is $Fe(OH)_2^+$.

Ferrous iron solubility is expressed by the following two equations in pure water at 25° C [17]:

$$Fe(OH)_2\ (s) = Fe^{2+} + 2\ OH^- \qquad \log k_{s0} = -14.5 \qquad (15)$$

$$Fe(OH)_2\ (s) = FeOH^+ + OH^- \qquad \log k_1 = -9.4 \qquad (16)$$

$$Fe(OH)_2\ (s) + OH^- = Fe(OH)_3^- \qquad \log k_2 = -5.1 \qquad (17)$$

Next, these equations are rearranged to develop the ferrous solubility diagram (figure 2):

$$[Fe^{2+}] = \frac{k_{s0}}{k_w^2}[H^+]^2 \qquad (18)$$

$$[FeOH] = \frac{k_1}{k_w}[H^+] \qquad (19)$$

$$[Fe(OH)_3^-] = \frac{k_2}{[H^+]}\ k_w \qquad (20)$$

Ferrous iron solubility occurs at high pH values. Maximum ferrous hydroxide concentrations occur at neutral and low pH where Fe^{2+} is the dominant species. At higher pH values, minimum ferrous hydroxide occurs and $FeOH^+$ is the dominant species up to approximately pH 12 where $Fe(OH)_3^-$ becomes the dominating species.

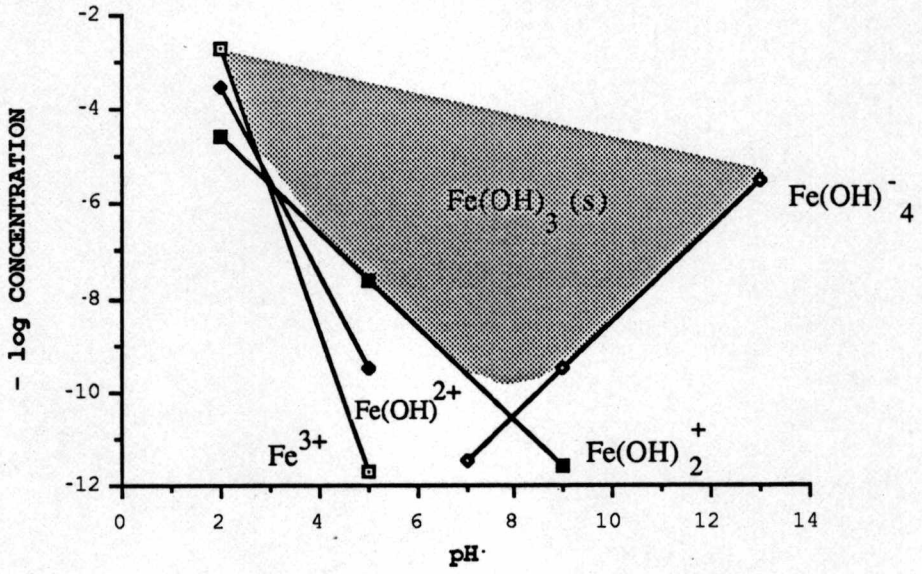


Figure 1. Ferric iron solubility diagram.

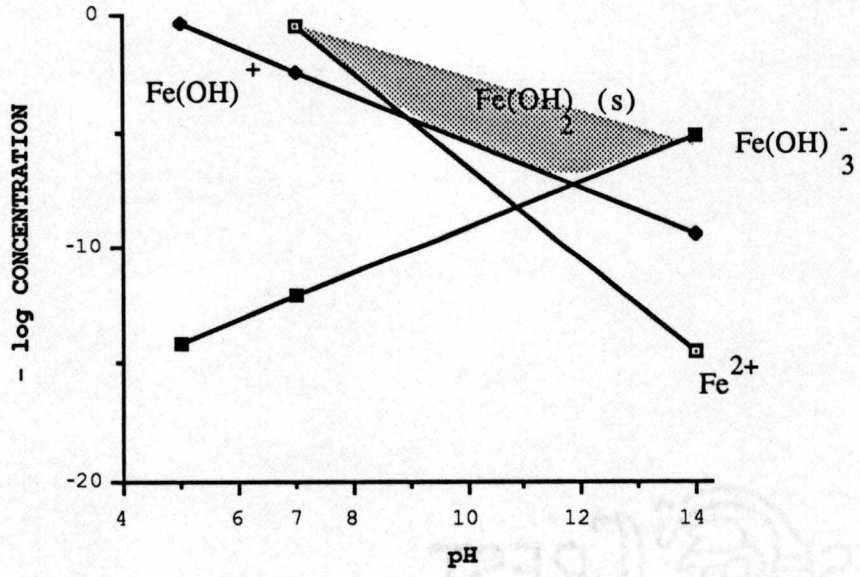


Figure 2. Ferrous iron solubility diagram.

Manganese (II) solubility can be expressed in the terms of $Mn(OH)_2$ (s) in pure water at 25° C [11]:

$$Mn(OH)_2\ (s)\ (active) + 2\ H^+ = Mn^{2+} + 2\ H_2O \qquad \log k_{s0} = 15.2 \quad (21)$$

Other equations of manganese solubility can be written as [11]:

$$Mn^{2+} + H_2O = MnOH^+ + H^+ \qquad \log k_1 = -10.6 \quad (22)$$
$$Mn^{2+} + 3\ H_2O = Mn(OH)^- + 3\ H^+ \qquad \log \beta_3 \approx -35 \quad (23)$$
$$Mn^{2+} + 4\ H_2O = Mn(OH)_4^{2-} + 4\ H^+ \qquad \log \beta_4 = -48.3 \quad (24)$$

These equations can then be rearranged as follows:

$$[Mn^{2+}] = k_{s0}\ [H^+]^2 \quad (25)$$
$$[MnOH^+] = k_1 k_{s0} [H^+] \quad (26)$$
$$[Mn(OH)_3^-] = \beta_3 \frac{k_{s0}}{[H^+]} \quad (27)$$
$$[Mn(OH)_4^{2-}] = \beta_4 \frac{k_{s0}}{[H^+]^2} \quad (28)$$

From these equations a solubility diagram for manganese can also be drawn (figure 3). Similarly to the iron solubility, maximum manganese solubility occurs at high pH values. At low pH Mn^{2+} is the predominant species and at low pH, $Mn(OH)^+$ and $Mn(OH)_3^-$ are predominant. As can be seen at neutral pH values, which are common to groundwater, manganese is soluble as $Mn(OH)^+$. In order for manganese to precipitate to insoluble $Mn(OH)_2$ (s) at neutral pH values, it must exist at uncommonly high concentration of 1*M* or more. At the MCL concentration of 0.05 mg/l, manganese becomes insoluble at a pH of 10.5. This supports the suggestion of the need for pH ≥ 9.5 by Viessmann and Hammer for manganese oxidation [2].

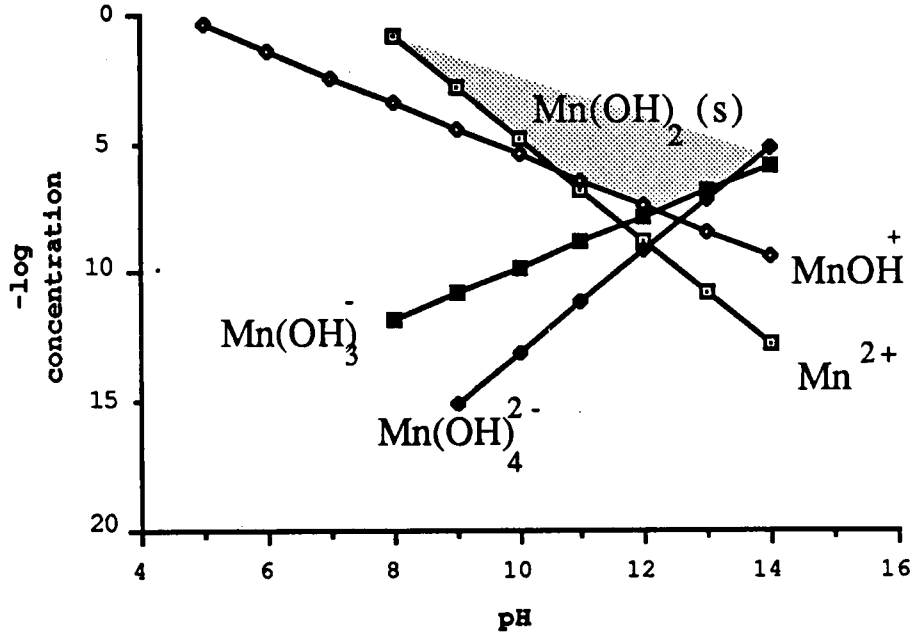


Figure 3. Manganese solubility diagram.

Aqueous Silicate Chemistry

Silicates comprise well over 90% of the earth's crust and nearly 40% of the common minerals are silicates [18]. The fundamental unit of silicates is a stable tetrahedron of O^{2-} surrounding one Si^{4+}, which is the center of the tetrahedron. The Si-O bond is very strong and is half ionic and half covalent [4]. The bonding strength is equal to one half the total available bonding energy, and, therefore, each O^{2-} can bond, or polymerize, with other tetrahedral units [18]. From polymerization arises various configurations of silicates such as orthosilicates, which have one tetrahedral unit, and sorosilicates, which have two units. Due to the various configurations, mineralogy of the silicates can range from high hardness and specific gravity in orthosilicates such as garnet to low hardness and specific gravity in biotite, a phyllosilicate which has three adjoining O^{2-} and the tetrahedral units are configured into flat sheets [18].

Silicate Solubility

Due to the abundance of silicates in the earth's crust, a high concentration of silica can be found in all bodies of water. Natural dissolved silica can commonly be found at 5-35 ppm as SiO_2 in rivers and streams and at 5-15 ppm as SiO_2 in sea water [19].

Soluble mono- or orthosilicate [4] is represented as $Si(OH)_4$ or H_4SiO_4. As $Si(OH)_4$ this emphasizes that metalloids such as Si, B, and Ge tend to coordinate with hydroxo and oxo ligands and form multinuclear species [11]. Multinuclear species of silica are commercially produced and used as synthetic clays, gels, anti-slip agents, dispersants, and deflocculants [4]. Orthosilicic acid is weak and nonionic in neutral and weakly acidic solutions but will ionize in alkaline solutions [6].

The following equilibrium equations represent the solubility of silica in a 0.5*M* solution of $NaClO_4$ at 25° C [11]:

$$SiO_2 \text{ (quartz)} + 2\ H_2O = Si(OH)_4 \qquad \log k_1 = -3.7 \qquad (29)$$

$$SiO_2 \text{ (amorphous)} + 2\ H_2O = Si(OH)_4 \qquad \log k_2 = -2.7 \qquad (30)$$

$$Si(OH)_4 = SiO(OH)_3^- + H^+ \qquad \log k_3 = -9.46 \qquad (31)$$

$$SiO(OH)_3^- = SiO_2(OH)_2^{2-} + H^+ \qquad \log k_4 = -12.56 \qquad (32)$$

$$4\ Si(OH)_4 = Si_4O_6(OH)_6^{2-} + 2\ H^+ + 4\ H_2O \qquad \log k_5 = -12.57 \qquad (33)$$

Equations 29-33 can then be modified and a solubility diagram for silica can be produced (figure 4):

$$Si(OH)_4] = k_1 \qquad (34)$$

$$[Si(OH)_4] = k_2 \qquad (35)$$

$$[SiO(OH)_3^-] = \frac{k_3 k_2}{[H^+]} \qquad (36)$$

$$[SiO_2(OH)_2^{2-} = k_4 \frac{k_3 k_2}{[H^+]^2} \qquad (37)$$

$$[Si_4O_6(OH)_6^{2-}] = k_5 \frac{k_2^4}{[H^+]^2} \qquad (38)$$

Quartz crystallizes very slowly at low temperatures [11] so therefore only amorphous silica and its equilibrium constant will be represented in the solubility diagram and equations. Silicic acid, $Si(OH)_4$, has a solubility of 120 ppm at neutral and slightly alkaline conditions and remains in the monomeric state, but under more alkaline conditions the soluble silica is in a multimeric state. At higher pH levels and concentrations greater than $10^{-2.7}\ M$ (120 mg/l as SiO_2), orthosilicic acid rapidly polymerizes into low molecular weight polysilicic acids and then further into colloidal polymeric particles [6]. At pH < 9.8 amorphous silica is formed but at higher pH the commercially important stable multimeric solutions are formed (shaded region).

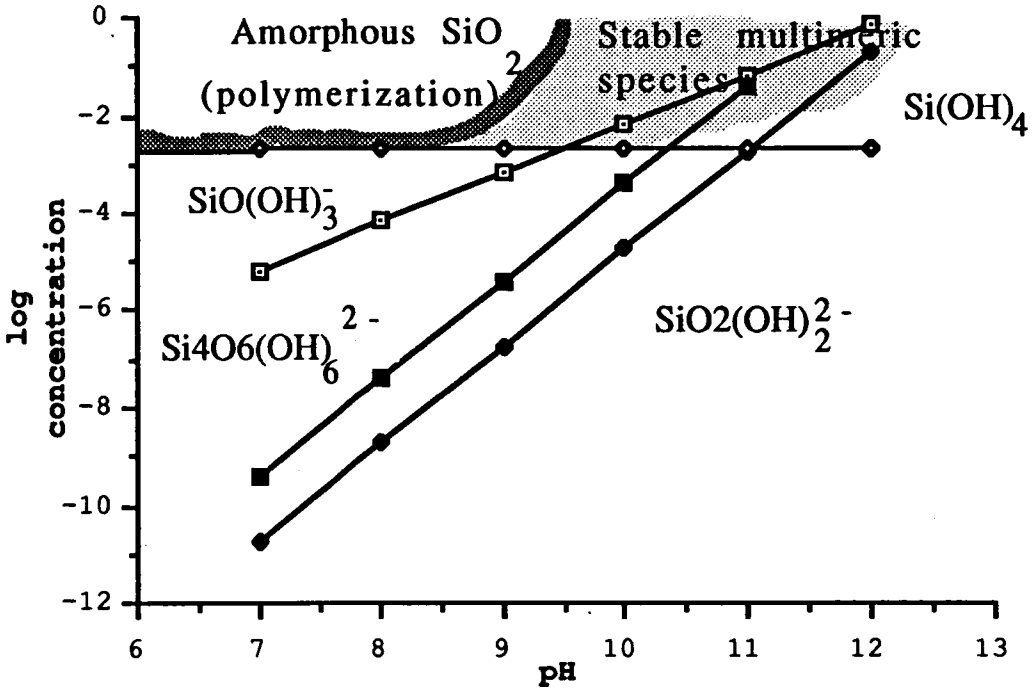


Figure 4. Silica solubility diagram. Adapted from Stumm and Morgan.

Commercial Sodium Silicate Solutions

Sodium silicates are commercially manufactured by fusing sand and sodium carbonate (soda ash) temperatures in excess of 1300° C [4]. The fused product is then dissolved in pressurized hot water and filtered [6]. The final product is a clear, or opalescent, concentrated alkaline solution with a SiO_2: Na_2O weight ratio, or m -ratio, of 0.5-4, where the most common commercial grade is a silicate solution with m = 3.22 [4,6]. Commercial applications of sodium silicate can be found in water treatment as deflocculants, dispersants, activated sols, synthetic clays, gels, zeolites, and anti-slip agents [4].

In water treatment application, sodium silicates are commonly diluted and/or reduced in pH during treatment. Changes in pH and concentration can place the solutions outside of the stable multimeric field and cause a change in the sodium silicate form. Sodium silicate will hydrolize into larger or smaller polymeric species [19]. A relatively stable solution can be achieved by rapidly diluting a 25% SiO_2 solution to 1% with simultaneous acidification to pH 2 at 0-5° C. Since this solution is in the insolubility range, it will eventually polymerize to amorphous silica [19].

Using the molybdic acid colorimetric test, O'Conner has shown that dilution of polymeric silicate (m = 3.3) decreased the level of polymerization as well as the total polymeric proportion [20]. McGarry and Hazel showed the effects of aging by the dilution of 10% 3.45 SiO_2: K_2O solution to 0.03% SiO_2. Direct dilution from 10% to 0.03% formed particles ranging from 1-5 nm in diameter. When dilution was stopped at 0.3%, aged, and then further diluted to 0.03%, the average diameter size was 8 nm [21]. Later experiments by Hazel [22] showed that the aged diluted solution would eventually produce similar distributions of low anionic microparticles to that of the direct diluted solution from 10% to 0.03%. Lehrman and Shuldener [23] also showed that increasing dilutions of 3.22 and 1.0 sodium silicate solution decreased the polymerization of silica which is evident by the increase of reactive silica to molybdic acid with each higher dilution. Polymerization of

silicate solutions is an important factor in sequestration. Therefore dilution of the solutions has an adverse effect on sequestration [6].

Interaction Of Silica, Iron, Manganese, And Other Metal Ions

To better understand iron and manganese sequestration, a discussion of silica interaction with these metals and other metal ions is needed. In natural groundwater systems, many dissolved metal species are present and may have an adverse or beneficial effect on treatment.

Most available information relates to the interaction of silica and iron. Equations have been developed to either conceptualize or quantify the iron-silicate reactions. Early work by Hazel, Schock, and Gordon [24] measured the drop in pH of acidic ferric and aluminum salt solution when titrated with fresh 2.5% silicic acid sols. the pH drop was apparently due to an exchange of ferric ions and hydrogen ions between the ferric solution and silicic acid. The drop in pH was lower than the initial pH of both the salt and acid solutions and the reduction of pH could not be duplicated by substituting stronger mineral acids. This proved that silica interacts with the iron. Silicate solutions aged from 45 hours to 10 days were less active due to polymerization which was indicated by a smaller decrease in pH. Upon aging of the sols, hydrogen ions are tied up which decreases reactivity. Two reactions were developed to conceptualize the interaction of silica and iron. The first is a one step reaction with unhydrated ferric iron:

$$n\,(\equiv SiOH) + Fe^{3+} \rightarrow [(\equiv SiOH)_n - Fe]^{(3-n)+} + nH^+ \qquad (39)$$

The second is a two-step reaction where the second reaction is believed to drive the first:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \qquad (40)$$

$$\equiv Si - OH + HOFe^{2+} \rightarrow \equiv Si - O - Fe^{2+} + H_2O \qquad (41)$$

The last equation is also believed by Hazel, Shock, and Gordon, but not proved, to discharge the iron color in alkaline conditions which is important in iron sequestration. It was noted that the greatest color discharge in ferric iron occurred with fresh acid. Similar tests with barium, lanthium, and chromic chlorides and copper sulfates insignificantly or slightly interacted with silicic acid sols.

Weber and Stumm [25] have quantified the interaction of silicic acid and iron by spectrophotometric measurements of iron silicate complexes at a wavelength of 272 nm. Freshly prepared silicic acid solutions at a concentration of $5 \times 10^{-2} M$ were mixed with dilute ferric perchlorite solutions. Absorbances were higher than iron alone solutions and pure silicic acid solutions have no absorbancy at this wavelength. A linear equation and an equilibrium quotient were developed when $[Fe^{3+}] < 5 \times 10^{-2} M$ for the iron-silica complex:

$$Fe^{3+} + Si(OH)_4 = FeSiO(OH)_3^{2+} + H^+ \qquad (42)$$

where Q = 0.57

A concentration stability constant was then derived at 25° C by combining Q with the first dissociation constant for $Si(OH)_4$ (3.2×10^{-10}):

$$K = \frac{Q}{K_{Si(OH)4}} = \frac{[FeOSi(OH)_3^{2+}]}{[Fe^{3+}]\,[SiO(OH)_3^-]} = 1.8 \times 10^9 \qquad (43)$$

Similarly, Olson and O'Melia [26] derived thermodynamic constants for equation 42:

$\Delta G^\circ = 0.80$ kcal/mole
$\Delta H^\circ = 3.73$ kcal/mole
$S^\circ = 9.83$ cal/mole deg

Their measurements of Q, both spectrophotometrically and polarographically, were 0.25 and 0.34 which are below the equilibrium constant of Weber and Stumm.

As mentioned before, silicic acid catalyzes the ferrous oxidation rate by molecular oxygen. Schenk and Weber [27] showed that silicic acid at concentrations from 0.1 to 1 mM is a catalyst in oxidation of iron at concentrations less than $5 \times 10^{-5} M$ at pH 6.7-6.9. Ferrous iron of the mixtures were analyzed by the bathophenanthroline method and data revealed that increasing silica concentrations increased oxidation. From this data constants for the effects of pH and silica concentration were obtained and then incorporated into the basic ferrous oxidation equation to get:

$$\frac{-d\ [Fe^{2+}]}{d\ t} = (K p_{O2} [OH^-]^2 + K_{Si} [H_4SiO_4]^{0.5} [OH^-]^{0.5} [Fe^{2+}] \qquad (44)$$

where $K = 2.1\ (\pm 0.5) \times 10^{13}$ L^2/mole^2 atm min

$K_{Si} = 1.8\ (\pm 0.3) \times 10^3$ L/mole

Additionally, Schenk and Weber noted that precipitation of ferric iron was retarded in the presence of silicic acid. At a pH of 3.5, 5.6 mg/l iron solution with 60 mg/l as SiO_2 of silicic acid had 7.5 times higher filterable iron through a 0.45 μm filter and with 6 mg/l as SiO_2 the filterable iron was 3 times higher.

In contrast to Shenk and Weber, $H_3SiO_4^-$ and other anions were found to slightly suppress the rate of oxygenation of iron (II) at pH 6.5 by Tamura et. al [28]. A 2 M iron (II) perchlorate solution was dosed with the anions along with 0.01 M Na_2HCO_3. A certain amount (no concentration given) of perchloric acid was added to prevent premature iron oxidation. At set time intervals, samples were collected and tested for ferrous iron by the 1, 10- phenanthroline method. From this data a rate constant was determined to be $1.63 \times 10^{14} / M^3$ sec.

Colloidal interaction of silica with iron is a primary factor in iron sequestration. Browman used ultrafiltration to show that the iron is contained in colloids [6]. This phenomena can be further detailed by looking at the particle surface charges.

Early work by Hazel [22] investigated the change in surface charge of iron oxide sols by sodium silicate solutions. Fresh sodium silicate solutions of 2000 mg/l as SiO_2 were diluted to 200 mg/l and then mixed with iron oxide sols at 80 mg iron oxide/l, which had been aged for one week. Hazel found that by pre-adjusting the pH to lower values, higher *m* -ratios of sodium silicate increase the negative charge of iron oxide surfaces at lower concentrations than do lower *m* -ratio solutions. Without pre-adjustment of the pH, lower concentrations of low *m* -ratio solutions rather than high *m* -ratio solutions increase the negative charge of iron oxide surfaces.

A hypothesis for the mechanism of sequestration can be formulated. The zero point charge for silica is pH 2.0 [11] and for iron oxides it is pH 8.6. From pH 2-8.6, silica has a negative surface charge and iron has a positive surface charge. The silicates will absorb to the iron forming negatively charged colloidal particles. A strong negative charge disperses the iron particles [29] reducing the tendency for precipitation. The pH_{zpc} for δ-MnO_2 (nsutite) is 2.8 [11]. At slightly alkaline conditions, its surface charge will be negatively charged which could repel the negatively charged silica. Besides slow oxidation rates, this may be another mechanism which hinders the sequestration of manganese.

Hazel also observed the effects of other metals on the interaction of silicate and iron. One-to-one electrolytes had no effect but $CaCl_2$ at 66.6 mg/l as Ca^{2+} increased the silica concentration needed to discharge the iron oxide surface. Other investigators [30] found that various sodium silicate solutions inhibit the crystallization of zinc ions. A potentiometric titration of zinc solutions with sodium hydroxide and sodium silicate solutions produced a series of titration curves with varying inflection points. As an example, the inflection point of $ZnSO_4$ was shifted over 100% of the equivalent base and increased as the silica concentration increased. Hazel et al. believe that the basic species are

being absorbed on the $Zn(OH)_2$ surface which produces the 100% shift in the inflection points.

Falcone examined the ability of sodium silicate to lower the activities of other ions [31]. *M* -ratios solutions of 0.5, 2.0, and 3.8, and a sodium hydroxide solution were mixed with Ca^{2+}, Mg^{2+}, and Cu^{2+} in chloride or perchlorate solutions. Increasingly higher *m* -ratio solutions caused greater activity reductions in Ca^{2+}. *M* -ratios of 2.0 and 3.8 had higher activity reductions in Mg^{2+} and Cu^{2+} but no significant difference between the two ratios were noted. During the study, Ca^{2+} and Mg^{2+} precipitation occurred immediately with high *m* -ratio solutions which is in contrast to the precipitation of Cu^{2+} which only occurred after aging of the mixture.

Iron and Manganese Sequestration

Iron Field Studies

Sequestering temporarily stabilizes iron and manganese in solution for a time which allows the treated water to pass through a distribution system. This treatment is mostly used in Ontario, Canada for the treatment of iron in small utilities, whereas only a few utilities in the US are sequestering iron. Manganese sequestration in British Columbia, Canada [32] provides some background information in the control of manganese by sodium silicate and chlorine which will be discussed later.

Some of the earliest work in iron sequestration was by Henry in 1950 [33]. A temporary measure to prevent iron flocculation of the Miami groundwater was needed until a conventional treatment plant was completed. Initial experiments were performed on unaerated groundwater samples taken from the well head which were dosed with polyphosphates and concentrated sodium silicate with an *m* -ratio of 3.22. Field tests were performed at a small system using similar water to Miami and was also suffering from red water problems. Best field and lab results occurred with sodium silicate whereas the polyphosphates showed poorer treatment and high turbidities. In the field sodium silicate

was diluted to a 3.2% solution and continuously dosed at 15 mg/l as SiO_2. Treatment, i.e. the iron was stabilized, only lasted three days under field conditions, which was half as long under comparable laboratory conditions. Activation of sodium silicate by bubbling with CO_2 gas before dilution improved treatment by 100%, but activation was not field tested for comparison.

Dart and Foley of the Ontario Ministry of Environment began a study of iron and manganese by accumulating field and laboratory data and literature to develop a better understanding of iron and manganese control in public water supplies [9]. In their work, they noted that groundwater with 30-40 mg/l SiO_2 held most of the iron after aeration or chlorination and even though iron concentrations ranged from 0.3-1.0 mg/l, consumers accepted the water with few complaints. Based on these findings and other investigations, such as the aforementioned by Henry, they decided to further investigate the sodium silicate-chlorine treatment as an alternative to conventional iron and manganese removal. The first field site was the town of Markham in February 1969, which was in need of an inexpensive, temporary solution to their red water problem before the anticipated connection to the Toronto water supply. Subsequent field tests soon followed at Markham Township, Bordon, and Gravenhurst. Raw water characteristics and treatment parameters of the four water supplies are compiled in Table 1 [4]. The water systems were all low in iron, neutral or slightly alkaline in pH, soft to medium hardness, and a silica background of 15-20 mg/l as SiO_2. In all cases silicate dosage occurred several seconds after chlorination. It was believed that silicate prior to chlorination would be unsuccessful due to the poor results of silicate treatment to the unchlorinated water at Gravenhurst. Research at UT has shown that better treatment occurs with silicate dosage before chlorination [4,6,29]. After two weeks of treatment, improvement in taste, cessation of staining, and a lack of red water due to deposited iron during flushing of the mains had occurred. Chemical costs at the

Table 1. Characteristics of Waters That Were Successfully Treated by Dart and Foley [4].

Characteristic	Water System			
	Markham	Markham Township	Bordon[c]	Gravenhurst
Iron, ppm Fe	0.5	0.2-0.7	0.40	1.45
pH	7.6- 8.0	7.7-7.8		7.1
Total Hardness, ppm CaCO3	150	300		96
Calcium Hardness, ppm CaCO3	98	220		55
Alkalinity, ppm CaCO3	200	b		56
Total Kjeldal, ppm N	1.4	0.54		b
Free Ammonium, ppm N	0.99	0.02		b
Nitrate, ppm N	a	0.02		0.014
Dissolved Solids, ppm	220	460		180
Sodium, ppm Na	24	22		12
Chloride, ppm Cl	15	55		b
Silica, ppm SiO2	19	20	15.0	19
Sulfate, ppm SO4	a	50		28
Phosphate, ppm PO4	a	0.12		b
Potassium, ppm K	a	1.7		3.6
Manganese, ppm Mn	a	0.0		b
Adequate Silica dose, ppm SiO2	2.7	4.6	5.4	6
Silica Feed Strength, % SiO2	28.7	28.7	20	c
Chlorination dosing point	just before silica addition	with silica addition	several seconds after silica addition	with silica addition

a Undetectable
b Not listed
c Identical to Markam Township except for ones listed

town of Markham were estimated at $1200/year (1969 dollars) whereas installation of an iron removal plant would have cost over $175,000 (1969 dollars).

Dart and Foley made the following conclusions with lab experiments conducted prior to and during their field studies:

1. Silicate stabilized iron best at pH ≥ 7.5.
2. Silicate-to-iron requirements were not linear. Higher iron concentrations needed increasingly higher silicate requirements.
3. Hardness increased silicate requirements.
4. Diluted or activated silicate was less effective than fresh, concentrated silicate.
5. Near simultaneous chlorination and silicate addition provided best results.
6. Rapid mixing and cold water improved iron stabilization.
7. High temperatures destabilized sequestered iron.
8. Manganese was stabilized more effectively than iron.

In a follow up report after 2 years of silicate-chlorine treatment, an arbitrary limit of 1.3 mg/l of iron was set by the Ontario Ministry of the Environment as the maximum feasible iron concentration for the silicate-chlorine treatment [10]. It was also decided to be impractical to treat very hard waters in this way due to lime precipitates which increased the feed pump maintenance. At that time, the maximum dosage was 6.2 mg/l as SiO_2. Manganese sequestration was thought to be highly dependent upon oxidation. Raising the pH in the presence of calcium ions appeared to increase manganese oxidation. Two side benefits of the treatment is a cleaning of the distribution mains and corrosion protection. In the town of Markham, a thin translucent coating was reported on the metal surfaces of the mains which clears tuberculated pipes and provides protection from corrosion.

Dart and Foley hypothesized that the formation of a silica-iron complex, $FeSiO(OH)_3^{2+}$, impeded the precipitation of ferric ions [9]. In their second report [10], their experiments suggested alternative explanations for impediment of iron precipitation.

Characterization of stabilized iron from on-site jar tests was attempted through ion exchange removal.

The iron was passed through strong and weak anionic resins of chloride and hydroxyl form and through strong and weak cationic resin of sodium and hydrogen form. All of the stabilized iron was removed by each of the anionic exchange resins and 100% of silica removal was obtained through the strong and weak base anionic hydroxyl resin. Iron removal through the cation resins was inconsistent and poor and silica removal was virtually zero. From these results, the iron-silica complex tends to be anionic rather than cationic as previously suggested.

Dart and Foley speculate that monovalent orthosilicate anions intervene with normal iron polymerization by suppressing the presence of positive catalysts in solution. Normal polymerization was suggested as:

$$Fe(OH)_2 \cdot 4H_2O^+ + Fe(OH)_4 \cdot 2H_2O^- \rightarrow (HO)_2 \cdot O \cdot Si(OH)_3 \cdot 5H_2O + H_2O \quad (45)$$

Orthosilicate was proposed to inhibit this reaction and complex with dihydroxyl ferric cations:

$$Fe(OH)_2 \cdot 4H_2O^+ + H_3SiO_4 \cdot 2H_2O^- + OH^- \rightarrow Fe(OH)_3 \cdot O \cdot Si(OH)_3 \cdot 6\,H_2O + H_2O \quad (46)$$

The iron-silicate complex was hypothesized to be unstable because of the presence of ferric precipitates.

In a later survey by Dart [34], 11 of 29 Nebraska filtration plants and 4 of 10 Ontario plants did not meet the minimal iron and manganese requirements after filtration. In Ontario, natural silica was interfering with the precipitation process. Sodium silicate sequestration could replace these systems and operate at 0.1% of the installation cost of a

filter plant. With sequestration, neither a skilled operator is needed except for maintaining chlorine demands nor is backwash needed.

Before determining the type of treatment Dart suggested that the following considerations should be made [34]: the presence of iron and manganese concentrations above secondary standards, the ease of oxidizing each contaminant, and the potential for biological fouling potential of the water. Chemical analysis for the following should also be made:

All nitrogens
Limestone saturation tests
Fouling factor components
Tracer ion tests
Field observations

Dart stated that sequestering is most susceptible to biological fouling by refractory organics which accelerate bacterial activity and by higher iron and manganese concentrations which lower the organic threshold for fouling. Traces of sulfide odor may indicate more efficient sequestration. Final treatment should be determined by on-site tests of the distribution system. Finally, Fe > 10 mg/l should be filter treated.

According to Dart four methods of sequestration is currently being used in Ontario [34]. Only procedures involving sodium silicate will be detailed.

1. Sodium Hexametaphosphate Procedure

2. Sodium Silicate Procedure I

   Dosage of 1-20 mg/l as SiO_2 (3.22) #B404-80 at 15 seconds before or after chlorination or aeration to treat 2.5-3.0 mg/l Fe. Dosage must be above hardness equivalents to sequester iron and manganese.

3. Sodium Silicate Procedure II

   Treats Fe ≤ 10 mg/l with 30-40 mg/l $CaCO_3$ by the following dosage of SiO_2 (3.22) #B404-80 and chlorination:

   $$\text{mg/l as } SiO_2 = [0.6\,[CaCO_3] + 1.07\,([Fe] + [Mn]) - [SiO_2]_{\text{raw water}}$$

4. Hydrogen Peroxide Procedure

   Maximum dosage in mg/l as H_2O_2 = 0.61 [Mn] for Mn ≤ 0.3 mg/l. Free chlorine will instantly oxidize H_2O_2 to free oxygen but reacts slowly with the manganese peroxide.

Three other observations were also made by Dart. Precipitated iron is not sequestrable. Continuous silicate injection provides better mixing then long-intervalled pulses as commonly seen with diaphragm pumps. Finally, thermal stratification of the water column hinders effective sequestration.

The Long Island Water Corporation (LIWC) is one of the few water utilities in the US that is practising iron stabilization by sodium silicate [35]. LIWC supplies a population of approximately 260,000 at an average consumption of 30 mgd. Most of the water is treated by filtration plants but, due to limited available land, filtration plants cannot be installed to service part of the system. The groundwater has a low pH of 4.7-5.5 and a varying iron concentration of 0.3-0.9 mg/l. To eliminate complaints of colored water, the sodium silicate treatment was employed after successful pilot studies which were conducted by Camp Dresser and McKee Inc.

Coloration of the water was due to iron deposits and corrosion products in unlined cast iron mains which were stirred up after frequent flow reversals. Annual flushing of the mains was practiced to minimize this effect. To stabilize the iron, sodium silicate (*m* -ratio unknown) at 4 mg/l as SiO_2 was added near-simultaneously with chlorine. The pH was adjusted to 7.5-8.5 which appeared to increase the efficiency of sodium silicate. Sufficient stabilization could be maintained at water heater temperatures of 70° C (160° F). After

treatment started in August 1971, complaints dropped 93% as compared to August 1970 statistics and a drop of 78% occurred in 1972 when compared the 1971 complaints.

Complex phosphate was also tested but sodium silicate proved to be the better stabilizing agent. Sodium silicate stabilized stabilized iron longer. It was more effective in the corrosion control pH range of 7.5-8.5. Thirdly, sodium silicate can not promote bacterial growth in the distribution system whereas phosphates are a nutrient and potentially could encourage bacterial growth.

Adjustment of pH to 7.5-8.5 for corrosion control was maintained by the addition of lime. As stated from earlier literature and experiments, calcium should have an adverse effect on iron stabilization. Therefore LIWC could possible increase the efficiency of sodium silicate stabilization by using an alternative method to increase the pH. Undiluted sodium silicate is a high alkaline solution and when used in treatment pH will naturally shift upwards. A possible alternative could be to increase the sodium silicate feed to higher concentrations in order to increase the pH of the groundwater. Sodium silicate may also coat the unlined mains which is an added measure against corrosion.

In a memo to Dr. Bruce Robinson from Camp Dresser and McKee, Inc.[12], the following findings were presented:

1. Iron stabilization was limited to iron and manganese concentrations of 1.5 and 0.8, respectively with soft New England groundwater.

2. Sodium silicate results were better at 140° F than at lower temperatures.

3. Turbidities below 2 NTU were acceptable if color and staining were reduced. Turbidities decreased with sample holding period.

These views are in contrast with lab results at UT. Iron has been successfully sequestered at concentrations as high as 2 ppm. Water characteristics of the New England

groundwaters which were not presented could be the probable cause of the lower iron concentration . Lab samples and field samples which had been heated to 59° C (138° F) showed poorer treatment, i.e. high turbidity and color and low iron filterability, then samples at 20° C. Finally, turbidities of lab samples increased over time. Iron particles can precipitate out of solution leaving a less turbid supernatent, but mixing will resuspend the particles. Mixing may be the difference in turbidity analysis between Camp Dresser and McKee results and the results of UT.

Iron Laboratory Studies

Robinson, Browman, and Reed [29], using a MINTEQ computer model, concluded that $FeOSi(OH)_3^{2+}$ could not account for sequestration due to insignificant concentrations at 2 mg/l Fe(II), 91 mg/l bicarbonate alkalinity, 19 mg/l SiO_2, and sufficient hypochlorite to oxidize the iron. If no iron was allowed to precipitate, then most of the iron was tied up in $Fe(OH)_2^+$ and $Fe(OH)_3$ while very little iron was predicted to complex with orthosilicate. They also concluded from their work that near simultaneous addition of sodium silicate and chlorine sequesters iron by dispersing an iron-containing colloid which grows slowly over time. They noted that large particles have a slower flocculation rate than smaller particles which implies that at a certain size range the iron flocs appear stable, i.e. sequestered, due to the very slow rate of flocculation. These particles are below the wavelength of light which will result in low turbidities. The primary role of chlorine is to oxidize the iron. The adverse effect of calcium ions follow the colloid stability theory and the Schultz-Hardy rule. Finally, due to rapid oxidation/hydrolysis of iron and rapid depolymerization of the sodium silicate, timing and mixing of the sodium silicate and chlorine is very important in the efficiency of treatment.

Robinson, Minear, and Holden [36] studied the effects of dissolved ions of calcium, sodium, sulfate, chloride, and bicarbonate on silicate-chlorine treatment of a model groundwater. The preparation of the model groundwater and procedures are very

similar to this thesis and will be outlined later. Sodium and calcium salts as sulfates, chlorides, or bicarbonate were added to the model groundwater prior to dosage of sodium silicate and chlorine.

Robinson, et. al. found that calcium increases the needed silicate dosage required to stabilize iron, which is in agreement with the hypothesis of Dart and Foley. In the presence of 25 ppm as $CaCO_3$, 16 ppm SiO_2 stabilized 2 ppm iron for less than five days whereas in the absence of calcium, iron stabilization occurred up to 10 days. Under similar conditions 25 ppm SiO_2 stabilized the iron for 10 days in the presence of 25 ppm $CaCO_3$ which is an increase of 1.6 times the required dosage. The calcium-silicate ratio was 1: 1.5 for this experiment. In another experiment at 10 ppm as $CaCO_3$, 16 ppm SiO_2 stabilized the iron for 10 days which gives a calcium to silicate ratio of 1: 2.7. Apparently the silica requirements are not linearly related to the calcium concentration.

From solubility studies of wallastonite and other calcium-silicate species, Robinson, et. al. determined that a calcium-silicate precipitate could not be the cause of increased silica dosage at the test pH levels and species concentrations. Very high concentrations of silica are needed for wallastonite precipitation and only insignificant trace amounts of other calcium-silicate precipitates would form under test conditions. Atomic adsorption of a filtrate which was passed through a 0.1 μm membrane filter and an unfiltered sample both had calcium concentrations close to the original calcium concentration of the model groundwater before dosage, which also supports the absence of calcium-silicate precipitates.

Other ions had negligible effects on the effectiveness of sequestration. Over 100% increases in the total sodium concentrations had very little effect upon the silicate requirement. Due to the similar results from additions of $CaCl_2$ and $CaSO_4$ as with NaCl and Na_2SO_4, the anions Cl^- and $SO42^-$ also had no effect upon treatment. Two experiments which increased and reduced alkalinity proved that HCO_3^- had negligible effects upon dosage as well. These results will allow predictions for the effects of other

ions. Like calcium, multivalent cations and polymers should adversely effect treatment whereas anions and monovalent cations should have little or no effect [36].

Robinson, et. al. also looked at increasing total ionic strength of the solutions as an indicator to iron precipitation. The ionic strengths of $NaHCO_3$, $FeCl_2$, NaOCl, $CaCl_2$, and $CaSO_4$ were measured in several experiments. If sequestering was dependent upon total ionic strength, then poor treatment would occur with high ionic strengths. No correlation between ionic strength and sequestration could be found and therefore They concluded that "ionic strength was not a reliable index of treatment effectiveness" [36].

Browman extended the research of Robinson, et. al. by studying the effects of lag-time between sodium silicate and sodium hypochlorite addition, of pH control, and of silicate dilution. Browman also prepared and treated a model groundwater with sodium silicate and sodium hypochlorite. His analysis also included iron ultrafiltration. His objective was to establish controlling factors in the sequestering treatment of iron of various silicate solutions at various dilutions [6].

To test the effects of lag-time, Browman varied the dosage of undiluted sodium silicate from 2.5 minutes before chlorination (as sodium hypochlorite) to two minutes after chlorination. Optimal conditions were when silicate was added 15 to 150 seconds before chlorination. Iron filterabilities were 95% or greater and turbidities were below 0.3 NTU. Lower iron filterabilities and higher turbidities occurred with simultaneous additions and with chlorination before silicate additions. The sodium silicate must be well mixed in the system before oxidation of iron takes place. Chlorine will oxidize iron which precipitates out of solution before the sodium silicate can take effect [37]. These findings contrast the works of Henry, Dart and Foley, and some field applications. All of the above chlorinated the water before addition of sodium silicate. Even though Dart and Foley suggest near simultaneous dosage (+/- 15 seconds), from personal communication, Mr. Dart suggests chlorination before the silicate addition. Through personal communication with F. E. Hale, Henry stated that treatment with sodium silicate before chlorination produced better results

at Jamaica, NY, which is consistent with Browman's work. Background silica in the raw waters could explain the successful treatment practice of chlorination before silicate dosage.

Next Browman examined the effects of controlling pH during treatment. Various dosages of concentrated and diluted silicate solutions were added under controlled and uncontrolled pH. Under controlled conditions, pH was reduced to 7.0 on each sampling day. Initial pH for controlled and uncontrolled conditions was 7.0. His findings indicated that higher pH levels reduced the required silica dosage and that diluted solutions were less effective under uncontrolled conditions. It was eventually decided to control the pH at 7.0 which would minimize pH variability, allow clearer distinction among various silicate performances, and allow for a more stringent test [6].

As stated earlier Browman found that dilutions of concentrated sodium silicate solutions decrease the effectiveness of treatment. Browman proved that polymerization was effected by dilution as well as the *m* -ratios of the sodium silicate solutions. The molybdic acid colorimetric test was performed on concentrated and diluted solutions of S35 (m = 3.75), N (m = 3.22), Star® (m = 2.50), and Starso® (m = 1.80), which are commercial grade sodium silicate solution provided by the Philadelphia Quartz Corporation. Higher *m*- ratios exhibited higher polymerization and diluted samples had lower polymerization than the undiluted samples of the same grade [6].Increasingly higher dilutions of various ratios of sodium silicate progressively reduced treatment effectiveness. Higher diluted *m* -ratios had better filterability then solution of lower *m* -ratios of the same dilution factor. This supports the idea that higher levels of polymerization of sodium silicate are more effective in treatment since dilution of sodium silicate decreases its polymerization.

Ultrafiltration of iron through either a 1000 or 200,000 molecular weight cut-off ultrafilters provided information of iron particle size distributions. Based on these measurements, the iron containing colloidal particles were very small but grew, or flocculated, over time. Sequestering apparently controls the growth, or flocculation, of the

particle. The most successful treatments showed the slowest rate of growth over time. Undiluted solutions exerted more control over particle growth then did $\frac{1}{100}$ diluted solutions.

Manganese Field Studies

In 1983, the City of Prince George, British Columbia, Canada commissioned a second pump station to meet current and expected future water demands [32]. A 1978 water quality survey showed that a high manganese concentration of 1.03 ppm was present which was a major concern of the water utility. Before the initial pump start-up, the city consulted Mr. Jim Dart for testing the water. He found that the manganese could be sequestered, albeit with difficulty. Otherwise the manganese was relatively stable and suggested that the use of perborate detergents over the use of chlorine based detergents to minimize the potential of laundry staining by manganese.

After the pump start-up, manganese levels dropped to 0.8 ppm but constant complaints of "brown or beige staining of laundry, white fencing and house siding, swimming pools, dishwashers, etc." were present from the moment of start-up. Initially the water utility encouraged consumers to use perborate type cleaners to minimize manganese oxidation possibilities, regularly and extensively flushed the distribution system, and advised consumers to clean stained laundry with a 50/50 mixture of hydrogen peroxide and white vinegar. The number of complaints dropped after mixing the water with a second water but complaints were still persistent and the mixing could only be a temporary solution.

Dr. W. F. Hyslop was later retained by the water utility to further test the effectiveness of manganese sequestration by sodium silicate. the fist test, consisting of three jar tests, was to determine the optimum sodium silicate dosage. Dosages at 0-10 mg/l as SiO_2 and 3-6 mg/l as Cl_2 were applied to freshly pumped raw water samples with a reaction time of 0.25-2.5 hours. The samples were then passed through fine porosity glass

filters and the field filtrate was taken to the laboratory. In the lab one-half of the filtrate was refiltered through a 0.45 μm filter. Ideally, if sequestration was occurring, then the filter would not be discolored as the sample passed through it. Hyslop determined sequestration was occurring when the silicate dosage ≥ 6 mg/l as SiO_2, 3 mg/l as Cl_2, and at long reaction times but at 6 mg/l as Cl_2 and very short reaction times no sequestering occurred.

A second experiment examined the qualitative impact on sequestered manganese from the additions laundry bleach, which is typically in a range of 100-200 mg/l as Cl_2, and the use of hydrogen peroxide as a sequestering agent. Six raw water samples were initially dosed with various combinations of sodium silicate, chlorine at 2 mg/l, and hydrogen peroxide also at 2 mg/l, and allowed to react for five minutes. Next, laundry conditions were simulated by adding 100 or 200 mg/l as Cl_2 and a visual/color observation test was conducted for one hour. A colorless solution could be maintained for 30 minutes at a dosage of 7 mg/l as SiO_2 and either Cl_2 and H_2O_2 or H_2O_2 alone. At these two dosages a pale yellow color developed after one hour. A dosage of 2 mg/l as H_2O_2 produced a pale yellow color in five minutes and further degraded to brown after 15 minutes. Simultaneous dosage of 7 mg/l as SiO_2 and 2 mg/l as Cl_2 stabilized the manganese. Addition of 2 mg/l as H_2O_2 with the above dosage produced an even more stable water.

After the sequestration treatment went on-line, a third test quantitatively simulated the impact of laundry bleach on sequestered water. Samples were dosed at 0-100 mg/l as Cl_2 and a reaction time of 0-60 minutes was allowed. Results suggested that no staining would occur during a wash cycle ≤ 10 minutes for a washing machine located at the pump station. Longer wash cycles would result in staining. Reaction times longer than 30 minutes allowed most of the manganese and iron to precipitate out of solution.

Sequestration was commissioned in 1985. The initial cost of installation was $160,000 with an operating cost of $45,000/year, or a unit cost of $35/MIG. Monthly rates were only increased by 5% (44¢/month). As a comparison capital costs for a typical

manganese removal system would have been $12,000,000 with operating costs of $135,000/year.

Complaints dropped to 4-5/month as compared to 65/month prior to sequestration. Since sequestration, most complaints are sporadic and come from isolated residential areas where laundry and dishwashers have been stained. Flushing will generally prevent staining but is not recommended during winter months. Another complaint is the gradual browning of light colored tiles and grout in swimming pools which can be cleaned by the 50/50 mixture of hydrogen peroxide and white vinegar.

After experiencing some problems with sequestering equipment, the water utility offers the following suggestions [31]:

1. "Avoid complicated valve switching on silicate feed lines using solenoid valves. The heat generated by the solenoid has a tendency to 'glass' the silicate in the valve, which quickly renders the valve ineffective."

2. "Emphasis should be placed on properly determining pump performance on a viscous liquid to avoid mechanical problems. Flooded suction recirculation and feed pumps are recommended. Progressing cavity chemical feed pumps were recommended through related pulp mill experiences and have performed well. Packing boxes, as opposed to mechanical seals, seem to give slightly better performance."

3. Recirculate silicate if the storage vessel is large relative to consumption.

4. "A stand-by feed pump and chlorine injector is recommended."

5. Maintain silicate at 16° C. If the liquid temperature drops, feed lines can be over pressurized and sodium silicate could freeze which does not reconstitute properly after thawing.

6. Use copious amounts of hot water and frequently place connection points on the pump systems for effective washdown.

Manganese Laboratory Studies

Robinson and Ronk [38] tested the effectiveness of N-sodium silicate (*m* -ratio = 3.22) and chlorine for stabilization of manganese. A model groundwater was prepared and a manganese concentration of 1-2 mg/l was obtained by adding manganese sulfate. Samples were dosed with sodium silicate and sodium hypochlorite nearly simultaneously and observed over a 10 day period.

They found that manganese could be successfully sequestered (turbidity $\leq$ 0.5 NTU and filterability > 90%) for up to one day but the best results occurred with no treatment of the manganese. Manganese is also not as treatable as iron with sodium silicate and chlorine. This could be due to the slow oxidation of manganese or to its negatively charged surface of manganese oxide. The pH_{IEP} of manganese is 2.8-4.5. Therefore at higher pH negatively charged manganese particles will hinder interaction with sodium silicate which is also negatively charged. Poorer treatment occurred at pH 8 than at pH 7. They hypothesized that manganese oxidation and hydrolysis is faster at pH 8 but still too slow to react with silica before the silica can depolymerize [38].

Even though no treatment of manganese in the laboratory prepared groundwaters give the best results, manganese field studies seem to differ with this point. In the aforementioned memo to Robinson, Camp Dresser and McKee, Inc. suspected that previously deposited manganese oxides in the mains catalyze manganese oxidation even in the absence of an oxidant. Under these circumstances, sodium silicate and hypochlorite, or silicate alone, provided better treatment.

The background of sequestration has two distinct divisions: laboratory studies and field studies. The laboratory studies provide objective insights to sequestration but this knowledge has not been proven in the field. Field studies are partly subjective and successful treatment has been found by trial and error, rather than by scientific methods.

Research is needed to combine these two divisions which will give field operators a better understanding of sequestration.

III. METHODS AND MATERIALS

Preliminary investigations involved the duplication of previous work by Browman and Holden. Upon successful duplication, further experiments were designed to study optimal iron sequestration conditions in the presence of calcium ions. The second step of the investigation involved field studies of four water utilities (Butler and Waukesha, Wisconsin and Aurora and Oak Ridges, Ontario) which are currently employing sodium silicate sequestration. A practice run was performed at the Ranielle, West Virginia water utility before the final field procedures were set.

Sequestration Of Model Iron Containing Groundwater

The following is the procedure for creating the model groundwater and treating it with N-sodium silicate and sodium hypochlorite:

1) Chill 22 liters of deionized, distilled, silicate-free water to 20 (± 2)°C for 18-24 hours. Check turbidity and temperature.

2) Sparge with pre-purified nitrogen gas at 20 L/min until the dissolved oxygen concentration < 0.1 ppm as O_2. Reduce sparge rate to ≅ 5 L/min.

3) After at least an hour of sparging, rapidly dissolve for 10 seconds, with stirrer on maximum, 5.544 g sodium bicarbonate in a 100 ml aliquot to provide an alkalinity of 150 ppm as $CaCO_3$ in the model groundwater. Allow 15 minutes for re-equilibration. Check pH and alkalinity. Acidify a 33 ml sample with one drop of concentrated double-distilled HNO_3 for analysis of background silica.

4) Adjust to pH 6.2-6.5 with CO_2 gas.

5) To a 100 ml aliquot of deionized water with a D.O. < 0.1 ppm as O_2, rapidly dissolve as above 0.1560 g $FeCl_2 \cdot 4\ H_2O$ and return to carboy to get 2 ppm Fe_2. Allow 15 minutes for re-equilibration.

6) Allow one minute for sparge gas to fill a 2-L plastic Nalgene jar. With a dispensing tube at the bottom of the 2-L jar, dispense two liters of the model groundwater into the jar.

7) Measure turbidity and pH.

8) Extract 20 ml and add to pre-made solution for Fe^{2+} analysis by the bathophenanthrolene method [38]. The pre-made solution consists of 4 ml of 10% solution of sodium acetate, 15 ml of 0.001*M* bathophenanthrolene, and three drops of double-distilled 6*N* HCl which were pre-mixed. Two ml of 10% hydroxyl HCl were added to reduce all iron to Fe (II) for total iron analysis. After 20 ml sample was added, 20 ml of hexyl alcohol were added. The bottle was shaken and then set aside to allow for seperation of the immiscible liquids. Analysis was made from the top red layer.

9) Add dosage of N-silicate to remainder and rapidly mix at 1000 rpm for 15 sec.

10) At t = 15 sec., let set 15 sec. with mixer off.

11) At t = 30 sec., add 7 ml of 0.1% sodium hypochlorite solution.

12) At t = 40 sec., mix at 1000 rpm for 45 sec.

13) Check turbidity.

14) Mix for 15 sec. at 1000 rpm. Take 20 ml for total iron. Acidify with 2 drops of 6*N* double-distilled HCl.

15) Take ≈ 50 ml for filterable iron. After all filterable samples are collected filter through a 0.1 cellulose membrane. Withdraw 20 ml and acidify.

16) Check pH and D.O. Extract 50 ml and dilute to 200 ml for free chlorine analysis. Take 33 ml and acidify with 1drop HNO_3 for silica analysis. Readjust to pH 7.0.

17) Fill head space with N_2-CO_2 mixture and place in shaker running at 1 rpm.

18) Rinse lid, mixer, and shaft with deionized silica-free water.

19) For each 2-L sample, repeat steps 7-19.

The pH is measured by an Orion Ross combination electrode and Orion ion meter. Sodium bicarbonate and ferrous chloride are rapidly dissolved on a stir plate. Turbidity is measured by a Hach turbidimeter. The dissolved oxygen concentration is measured with a Yellow Springs, Inc. (YSI) oxygen meter along with an YSI submersible oxygen probe. Total and filterable iron and silica analysis are made according to the sixteenth edition of *Standard Methods* [39] on an Instrumentation Laboratory AA/AE spectrophotometer. Ferrous iron analysis is made on the Perkin-Elmer Hitachi 200 spectrophotometer using a modified version of the bathophenanthrolene method proposed by Lee and Stumm[38]. Alkalinity is determined titrimetrically using 0.02*N* H_2SO_4 and titrating to the methyl orange end point. Free chlorine is measured by a Fisher chlorine titrimeter. At times when the titrimeter was down, colorimeteric measurements were made on a Hach field kit.

On days 1, 3, 5, and 10 samples are taken with a wide-tipped pipet for measurements of turbidity, total iron, and filterable iron.

1) Measure pH.
2) Mix for 30 sec at 1000 rpm.
3) Mix for 10 sec at 500 rpm.
4) Withdraw 25 ml for turbidity.
5) Mix for 10 sec at 1000 rpm.
6) Withdraw 20 ml for total iron and acidify with 2 drops HCl.
7) Withdraw ≈ 50 ml for filterable iron. Filter through a 0.1 μm filter and acidify

20 ml of filtrate with 2 drops of HCl.

8) Adjust to pH 7.0 with CO_2.
9) Refill head space, recap 2-L bottle, and replace it into the shaker.
10) Repeat steps 1-9 for all 2-L samples.

Optimization In The Presence Of Calcium Ions

The above procedures were followed in this phase of the investigation with a few modifications. Various concentrations of $CaCl_2$ were individually added to each 2-L sample for a range of 0-200 ppm as $CaCO_3$ except for experiment 17 where 155-157 ppm as $CaCO_3$ was added to the 22-L carboy. In experiment 14, the pH was raised to 8.0 immediately after dosage for one-half of the bottles. The test period was reduced to 5 days which is a more realistic residence time of treated water in the distribution system.

Calcium analysis was conducted according to the Sixteenth edition of *Standard Methods* [39]. A 33 ml sample was acidified with double-distilled HNO_3. A 20 ml sample was then extracted and diluted with 2 ml of lanthium oxide solution. Analysis was performed on the AA/AE spectrophotometer.

In each laboratory experiment, all 2-L bottles contained at least 90% ferrous iron unless otherwise noted. If 90% ferrous iron was not present in most of the bottles, then the experiment was repeated. A table of results for each experiment lists the ferrous iron percentages for all bottles.

Field Procedures

Field procedures were based on the practice run conducted in Ranielle, W. Va. Six 2-L samples were collected at various points in the water system. Raw water was collected at the pump head which represents a control sample. Three samples were collected at the pup station immediately after treatment. One sample was to be placed in a water bath at ≈ 59° C and the second was to be controlled at pH 7.0 on day 1, while the third was to be left

alone. The last two samples were collected from the distribution system. One was to represent a near point in the system while the other represented a distant point.

At each site, chemical analysis for free chlorine, dissolved oxygen, color, and turbidity were made using a Hach field kit. Temperature and pH were taken by a pH field probe. Samples were collected and preserved for total and filterable iron, ferrous iron, calcium, magnesium, total and filterable manganese, and alkalinity.

Samples were brought back to UT on the following day where further samples were collected over time for iron and manganese. As previously mentioned, one sample was placed in a 59° C water bath and another was reduced to pH 7.0 by sparging with nitrogen gas. In the lab, ultrafiltrations were carried out by passing the iron and manganese through a 1000 MW cut-off filter. Since most utilities use 0.45 μm filters, it was decided to incorporate these filters into the Ontario field tests. Free chlorine, color, turbidity, pH, and temperature were recorded on each sampling day.

IV. RESULTS

The discussion of the results will be divided into two sections. The first will be a discussion of the lab results and the second will be a discussion of the field results. In the field results a case history of each utility will be presented.

Optimization In The Presence Of Calcium

Holden found that 16 mg/l SiO_2 could only stabilize 2 mg/l of iron for less than five days when 25 mg/l $CaCO_3$ was present, whereas without calcium, stabilization occurred for 10 days. Experiment 1 tested the sequestering ability of 12-13 mg/l SiO_2 with 0-175 ppm $CaCO_3$ (Table 2). When no calcium is present 12 ppm SiO_2 will stabilize iron for up to three days (figure 5), but when 44 ppm $CaCO_3$ or more is added, stabilization occurred for only one day or less. Even though stabilization occurred in the presence of 8.4 ppm $CaCO_3$, iron filterability was less on days 1 and 3 than iron filterability without calcium. The uncontrolled pH sample exhibited less filterability than its counterpart which was maintained at pH 7.0. Both had 44 ppm $CaCO_3$, but only the pH-controlled sample had greater than 90% filterability by day 1. All iron samples that were successfully stabilized (filterability $\geq$ 90%) had turbidities lower than 0.4 NTU (figure 6). As filterability decreased, an increase in turbidity occurred. The drop in filterable iron and increase in turbidity over time emphasizes the fact that sequestering is only a temporal effect. The pH of all controlled samples naturally rose above 7.0 but was reduced back to 7.0 on each sampling day (figure 7). The uncontrolled pH sample was initially at pH 7.5 and then allowed to drift over the test period. Three samples dropped to below pH 7.0 on day 5 which could be attributed to excess sparging with nitrogen gas. Total iron was relatively constant for all samples except for the undosed sample (figure 8).

In test 2, iron stabilization in the presence of 0-188 ppm $CaCO_3$, the silica dosage was inadvertently doubled to $\approx$ 26 ppm as SiO_2, which is higher than typical water

Table 2. Five-day results of test 1 in which approximately 2 ppm iron was dosed with 12.3 - 13.6 ppm as SiO2[a]

Sample[b]	CaCO3 (ppm)	Day 0				Day 1				Day 3				Day 5			
		Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH[c]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH
10	0	75	1.99	1.3	7.0	27	1.83	1.2	6.8	18	1.86	1.2	7.2	62[d]	1.01	1.2	7.0
11	0	98	1.91	0.25	7.0	99	1.91	0.30	7.1	99	2.03	0.32	7.2	1	2.00	0.66	6.8
12	8.4	99	2.00	0.26	7.0	98	1.99	0.28	7.2	93	2.05	0.37	7.0	3	2.03	0.64	7.2
13	44.1	98	2.05	0.24	7.0	90	2.02	0.28	6.8	12	2.00	0.57	7.3	2	2.01	0.64	6.8
14	44.4	99	2.05	0.27	7.5	63	2.03	0.46	7.5	5	2.02	0.65	7.8	0.5	2.05	0.67	7.7
15	89.1	80	2.05	0.43	7.0	92	2.03	0.60	7.1	2	2.01	0.98	7.3	3	2.01	1.0	6.6
17	174.2	8	2.05	0.58	7.0	3	2.02	1.0	7.4	0.5	2.01	1.2	7.0	0.5	2.02	1.2	7.1

Alkalinity = 150 ppm as CaCO3 to the methyl orange end point.

[a] Sample 10 is the raw sample which is not dosed with sodium silicate.

[b] All samples were greater than 90% ferrous iron.

[c] The pH of all samples were adjusted to 7.0 on each sampling day except for sample 14.

[d] The total iron sample was mistakenly filtered before analysis causing the high reading.

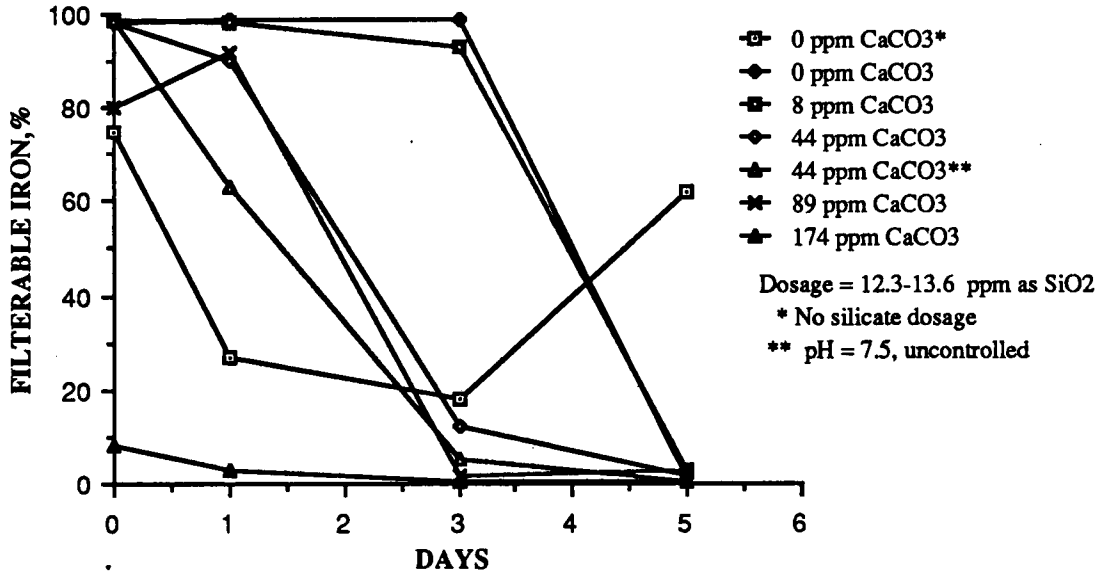


Figure 5. Filterable iron of samples from Test 1.

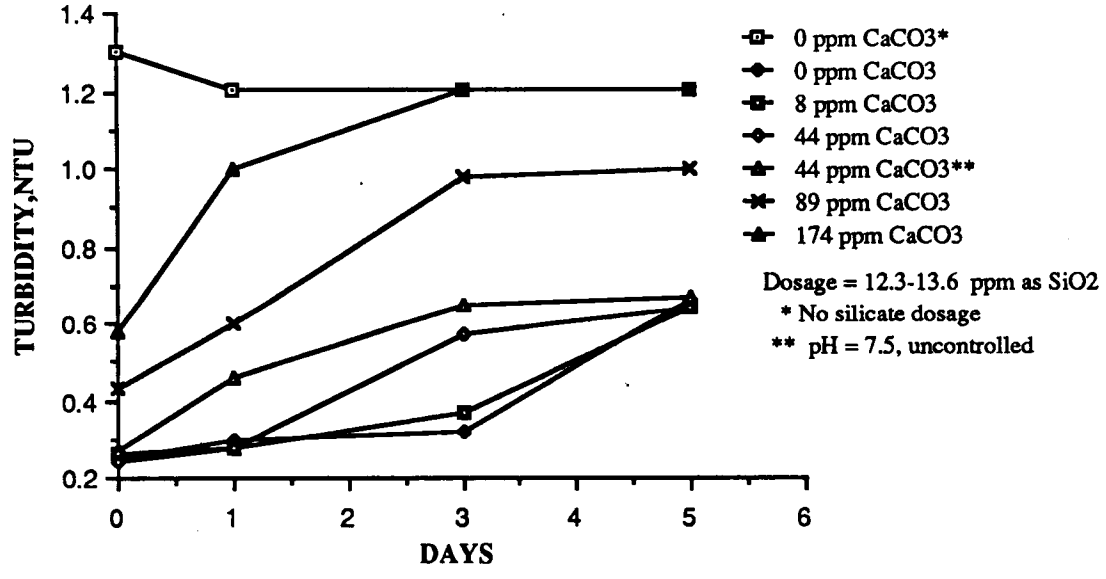


Figure 6. Turbidity of samples from Test 1.

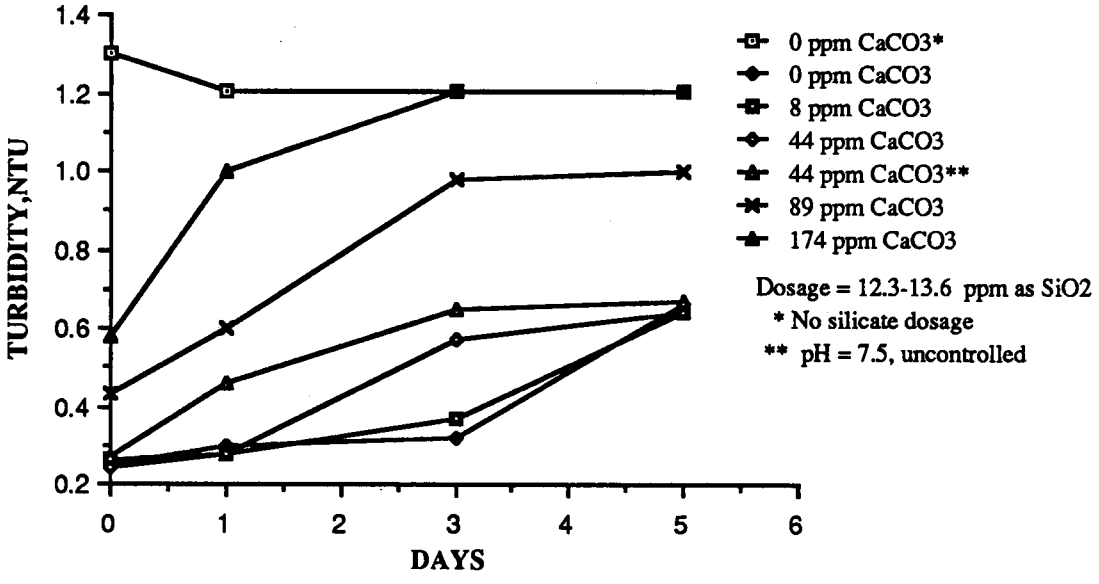


Figure 7. pH of samples from Test 1.

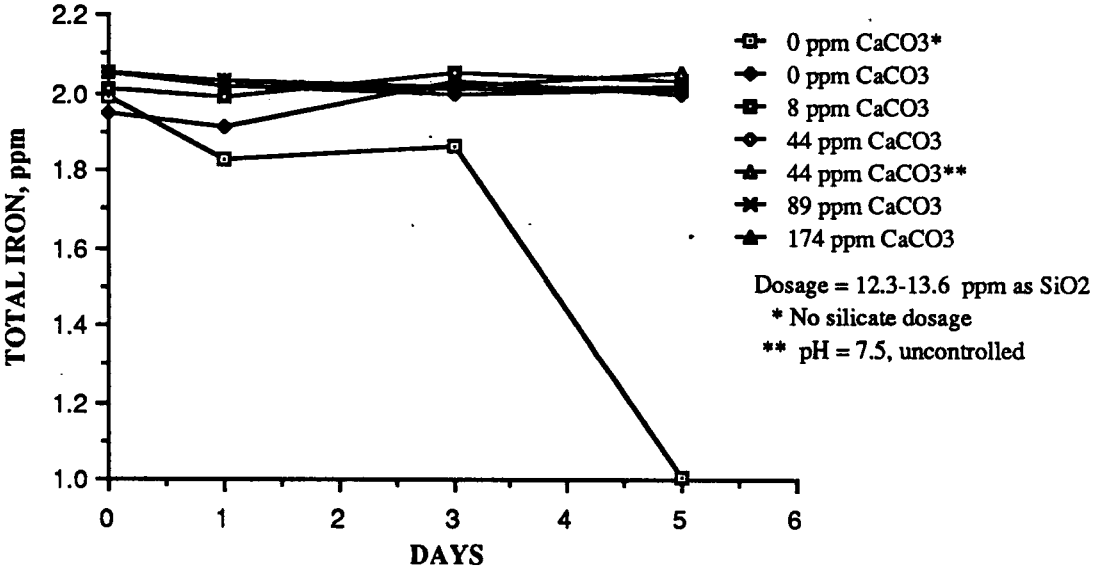


Figure 8. Total iron concentrations of samples from Test 1.

treatment dosages. At 26-28 ppm SiO_2, iron can be stabilized for up to five days in the presence of 45 ppm $CaCO_3$ or less (table 3). Iron filterabilities were greater than 95% through day 5 for samples with 45 ppm $CaCO_3$ or less (figure 9). Raw water filterabilities were higher than poorly treated samples in some instances which was believed to to be due to breakup and resuspension of the iron precipitate during mixing. For the stabilized samples, turbidities $\leq$ 0.4 NTU existed (figure 10). As with test 1, the pH was controlled at 7.0 with one exception, where a sample was allowed to drift in pH (figure 11). At 93 ppm $CaCO_3$, the iron was stabilized for less than one day and turbidities were higher than the stabilized samples. The sample with uncontrolled pH had greater than 90% filterability only through day 1. As with the previous test, total iron concentrations were relatively stable except for the undosed sample (figure 12).

The pH was the controlling parameter for iron stabilization in test 3. A dosage of 20 ppm as SiO_2 was injected with a range of 14-170 ppm $CaCO_3$ present (table 4). The pH of each solution was controlled at either 7.0 or 8.0 (figure 13). According to Browman [6], the best results should occur at pH 8.0. Unexpectedly, the solutions at pH 7.0 were better. The dosage of 20 ppm SiO_2 stabilized over 95% of the iron for five days with 14-48 ppm $CaCO_3$ (figure 14). At pH 8.0, filterability dropped to below 90% after day 1. In this calcium range, there was an insignificant difference in turbidities for both pH levels (figure 15). Stabilization occurred only for one day or less at higher $CaCO_3$ concentrations except for the sample at pH 7.0 and 88 ppm $CaCO_3$ in which stabilization lasted for three days. Turbidities were generally higher for solutions at pH 8.0 than their pH 7.0 counterparts. The total iron concentration for all samples was relatively constant through five days (figure 16).

Table 3. Five-day results of test 2 in which approximately 2 ppm iron was dosed with 25.4-28.0 ppm as SiO_2 [a]

Sample [b]	$CaCO_3$	Day 0				Day 1				Day 3				Day 5			
		Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH [c]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH
10	0	12	2.18	1.2	7.0	71	2.09	1.2	6.8	12	2.03	1.1	6.5	10	1.98	1.1	7.2
11	0	97	2.16	0.45	7.0	100	2.16	0.38	6.9	99	2.19	0.37	7.2	65	2.18	0.55	7.3
12	8.3	99	2.17	0.33	7.0	98	2.20	0.36	6.9	99	2.22	0.38	7.1	97	2.24	0.41	7.3
13	44.8	99	2.19	0.29	7.0	98	2.21	0.31	6.7	98	2.22	0.37	7.0	96	2.23	0.44	7.2
14	44.5	98	2.18	0.35	7.0	99	2.21	0.36	6.8	80	2.24	0.57	7.6	6	2.23	0.81	7.7
15	93.0	99	2.17	0.35	7.0	20	2.22	0.41	7.2	26	2.23	0.84	7.2	4	2.18	0.88	7.3
17	188.0	97	2.18	0.40	7.0	71	2.22	0.68	7.2	6	2.20	0.98	6.8	3	2.18	1.0	7.3

Alkalinity = 169 ppm as $CaCO_3$ to the methyl orange end point.

[a] Sample 10 is the raw sample which is not dosed. Samples 11 and 14 had only 9.5 and 18.6 ppm as SiO_2, respectively.

[b] All samples were greater than 92% ferrous iron except for sample 10 which was 88% ferrous iron.

[c] The pH of all samples were adjusted to 7.0 on each sampling day except for sample 14.

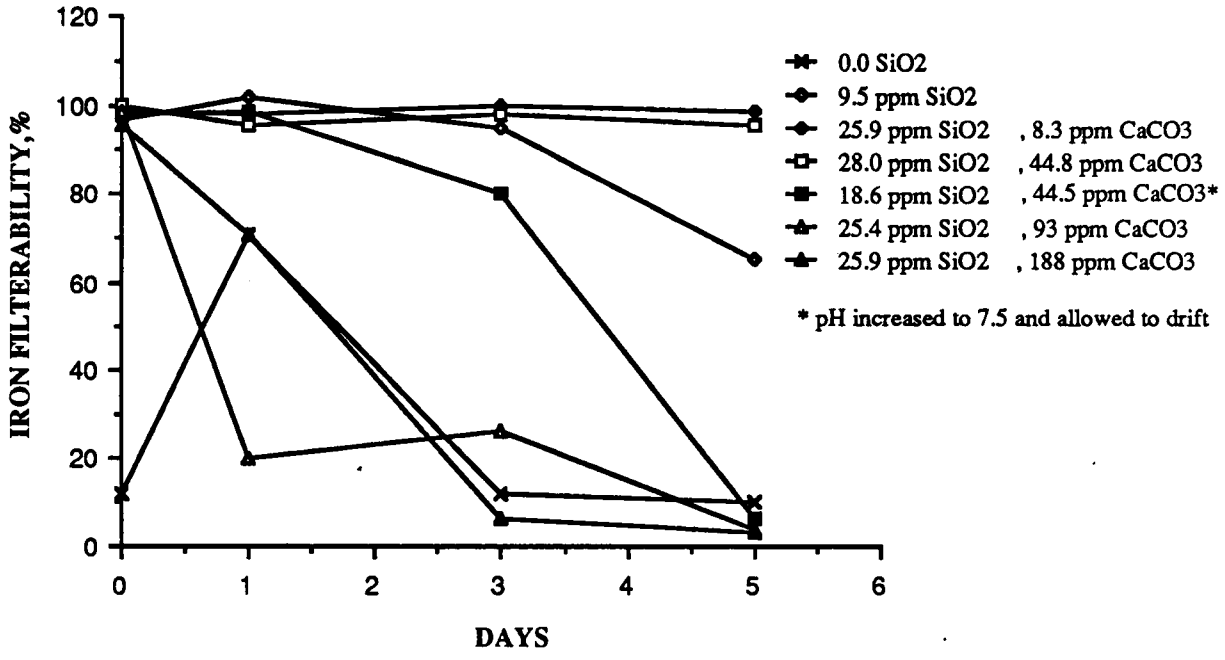


Figure 9. Filterable iron of samples from Test 2.

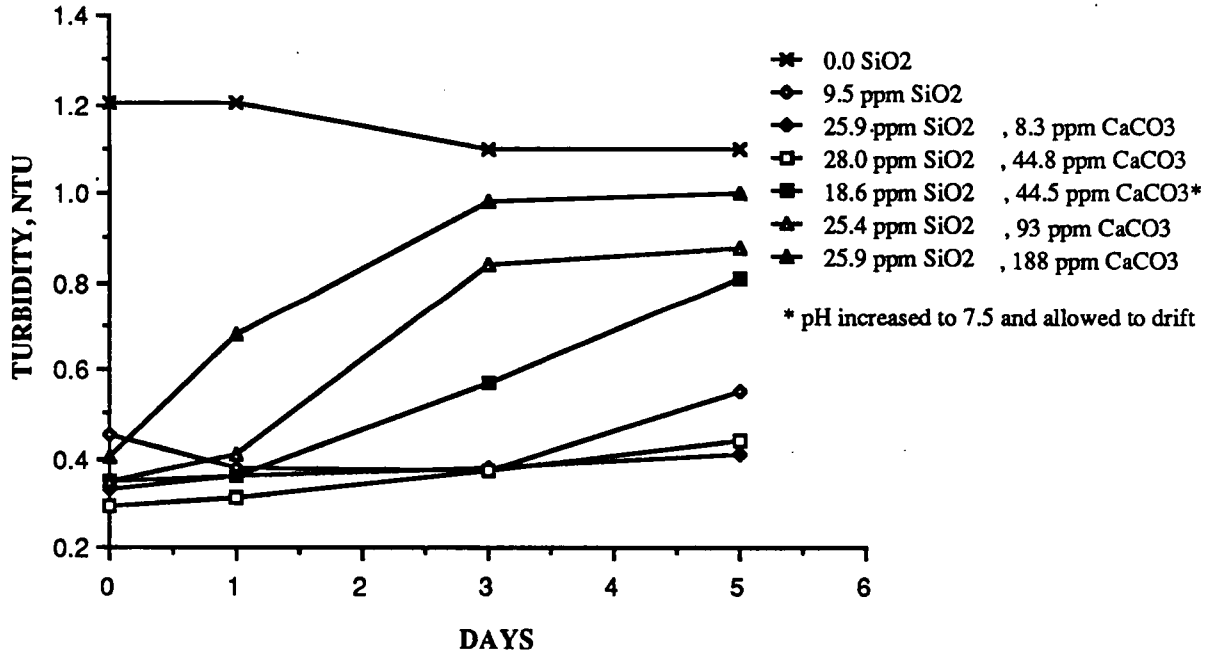


Figure 10. Turbidity of samples from Test 2.

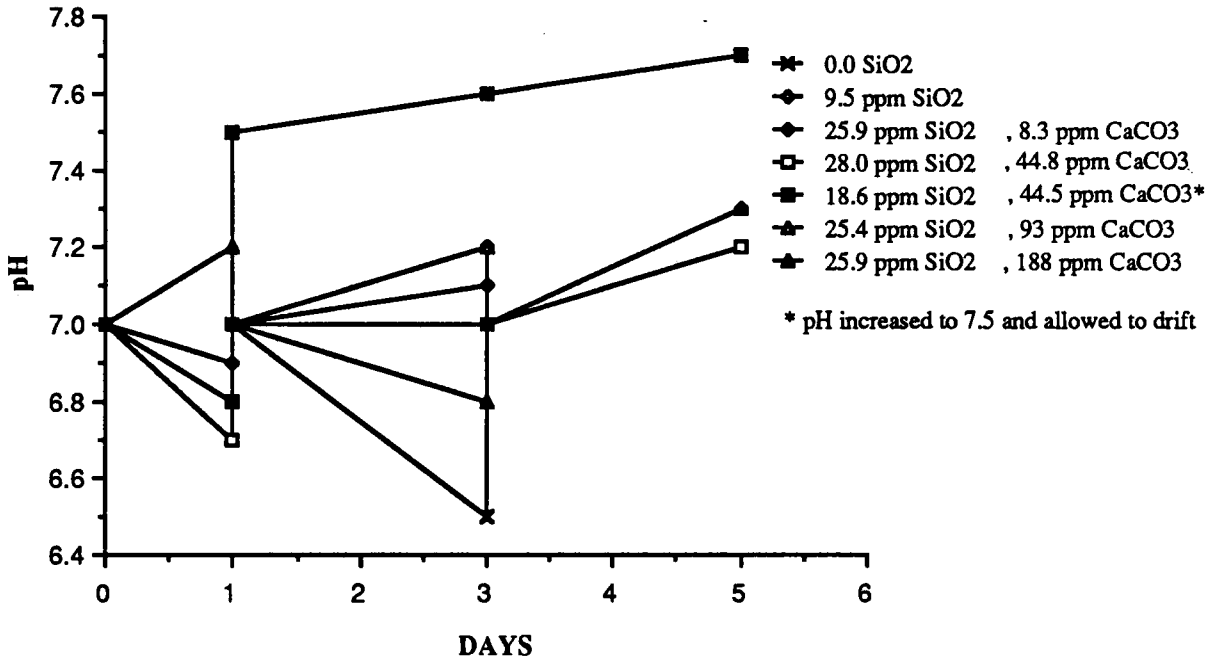


Figure 11. pH of samples from Test 2.

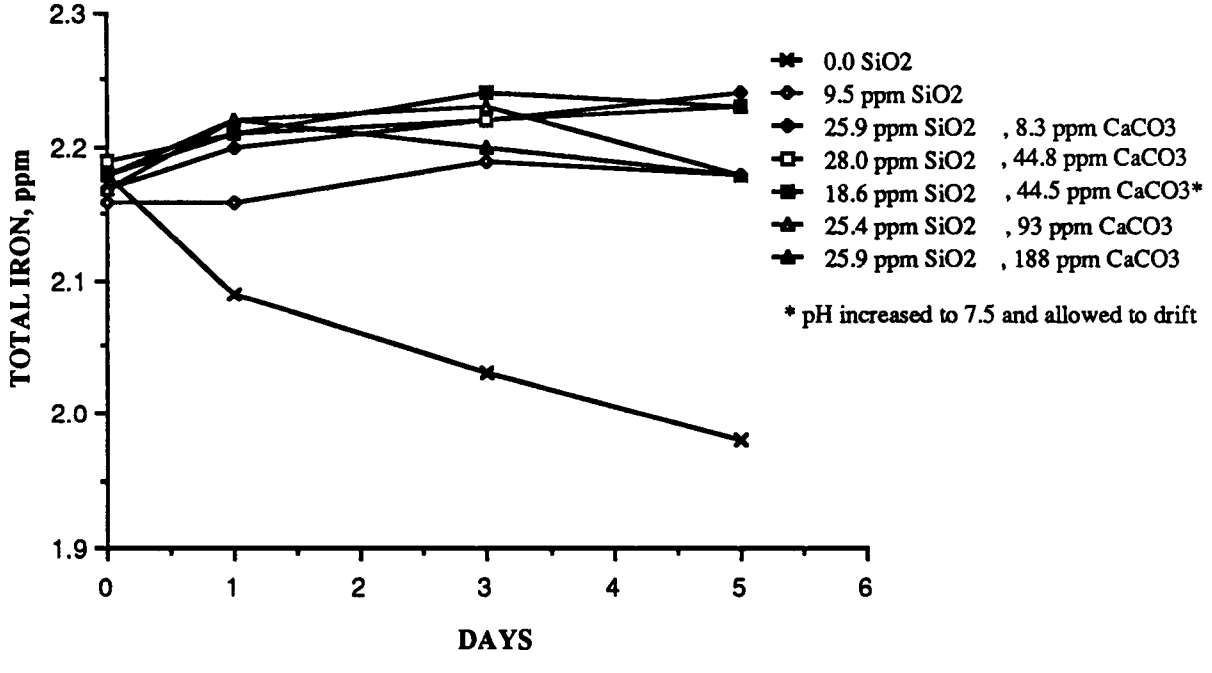


Figure 12. Total iron concentrations of samples from Test 2.

Table 4. Five-day results of test 3 in which approximately 2 ppm iron was dosed with 20.1 - 21.0 ppm as SiO_2 [a]

Sample [b]	$CaCO_3$	Day 0				Day 1				Day 3				Day 5			
		Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH [c]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH
10	14.0	90	2.05	0.45	8.0	91	2.02	0.53	8.4	85	2.03	0.68	8.0	87	2.03	0.64	8.2
11	14.0	96	2.09	0.28	7.0	97	2.07	0.34	7.0	98	2.06	0.35	7.1	96	2.05	0.32	7.4
12	47.5	91	2.07	0.40	8.0	91	2.02	0.48	7.2	88	2.02	0.65	7.5	74	2.02	0.67	7.7
13	48.2	99	2.05	0.27	7.0	97	2.04	0.28	7.1	98	2.04	0.30	7.2	95	2.05	0.37	7.4
15	87.8	79	2.01	0.57	8.0	69	1.99	0.98	7.8	4	1.99	1.0	7.3	3	1.98	1.0	7.9
16	88.0	97	2.05	0.25	7.0	97	2.06	0.35	7.2	97	2.04	0.37	7.1	4	2.05	0.62	7.3
17	170.0	4	2.02	0.49	8.0	91	2.03	0.66	7.2	3	2.00	1.0	7.6	4	2.02	1.0	7.9
18	169.0	96	2.06	0.40	7.0	97	2.06	0.51	7.5	3	2.00	0.77	7.4	1	2.03	0.85	7.4

Alkalinity = 169 ppm as $CaCO_3$ to the methyl orange end point.

[a] All samples were dosed.

[b] All samples are greater than 93% ferrous iron.

[c] The pH of samples 11, 13, 16, and 18 were adjusted to 7.0 while samples 10, 12, 15, and 17 were adjusted to 8.0 on each sampling day.

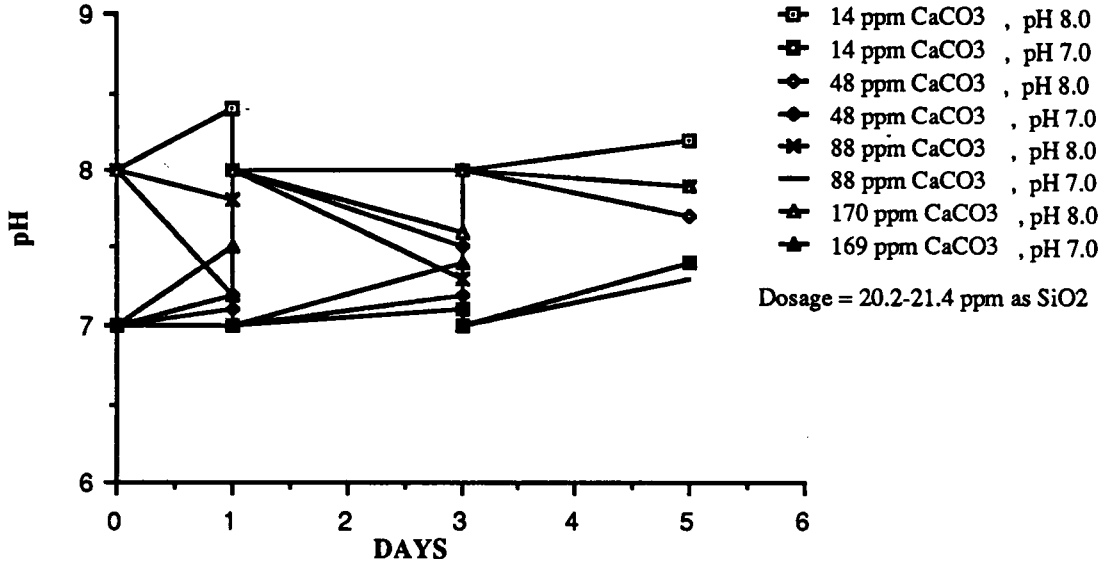


Figure 13. pH of samples from Test 3.

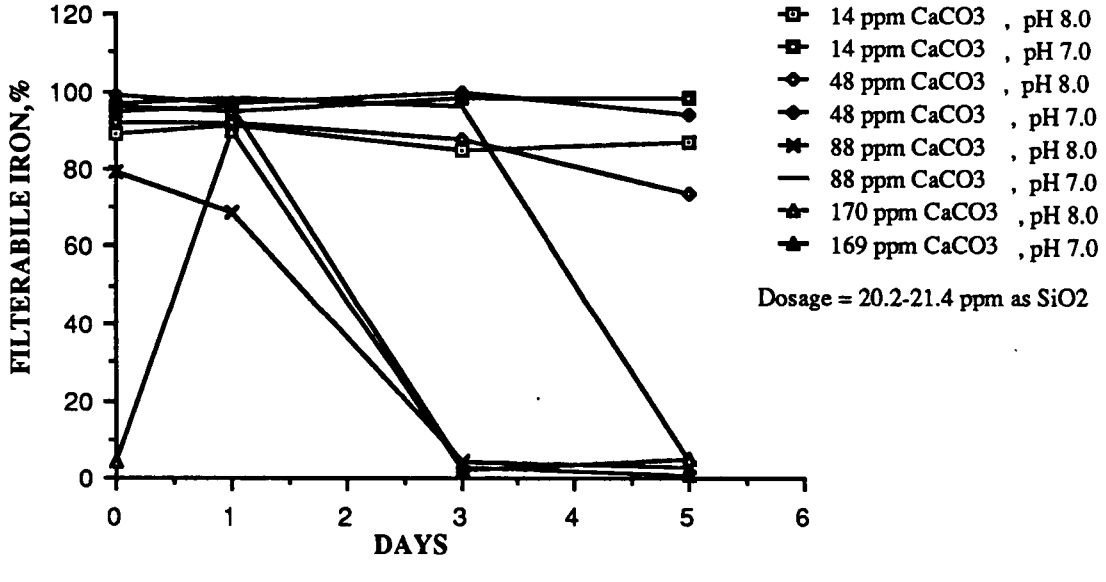


Figure 14. Filterable iron of samples from Test 3.

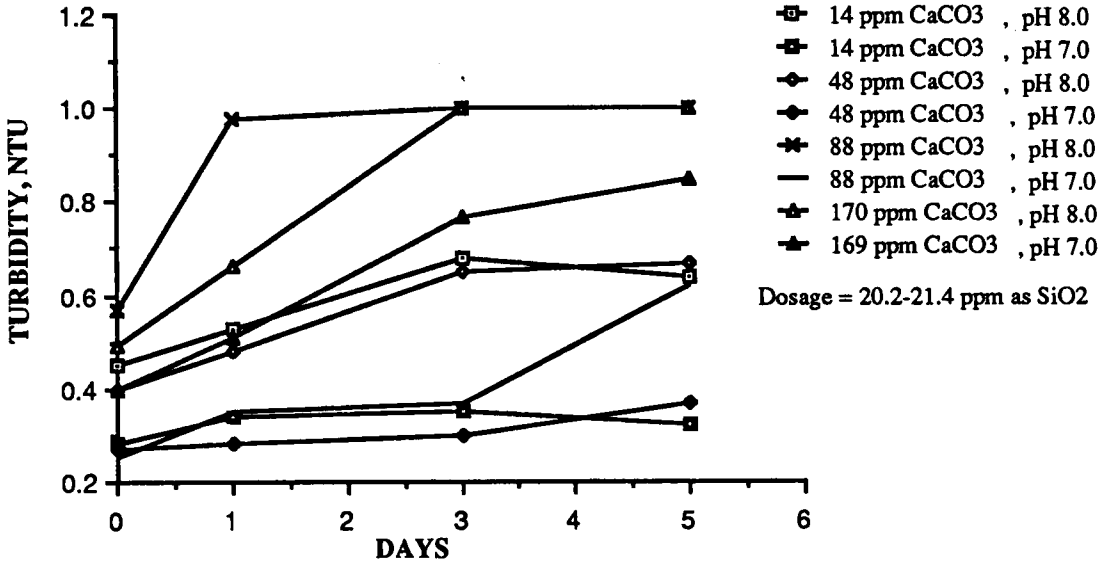


Figure 15. Turbidity of samples from Test 3.

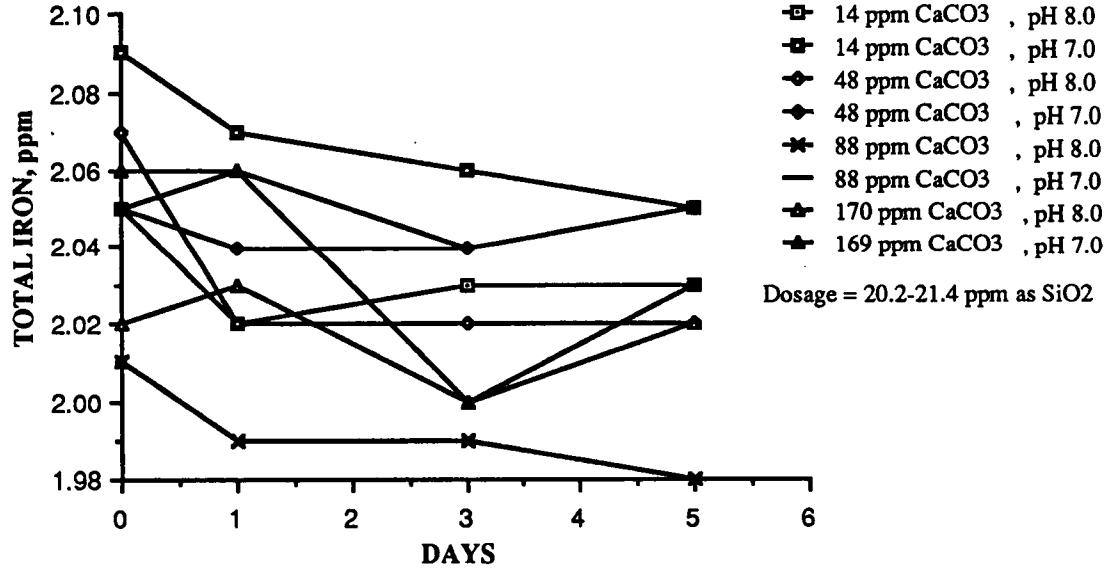


Figure 16. Total iron concentrations of samples from Test 3.

As a follow-up to these comparisons various dosages of sodium silicate from 0-37.6 ppm as SiO_2 at pH 7.0 or 8.0 were tested in the presence of 155-157 ppm $CaCO_3$ to corroborate the pH findings in test 3 (table 5). Naturally, the higher silica dosages exhibited better treatment. A dosage of 37.6 ppm SiO_2 at pH 7.0 stabilized the iron for up to five days. Iron filterabilities > 90% (figure 17), turbidities < 0.32 NTU (figure 18), and relatively constant total iron (figure 19) occurred through day 5. One interesting observation is that a slightly lower dosage of 33.4 ppm SiO_2 at pH 8.0 stabilized the iron only up to day 1. Iron filterability was 98% but dramatically dropped to 4% by day 3. Silicate dosages from 11.4-27.9 ppm as SiO_2 stabilized the iron only on day 0 for both pH 7 and 8. Thereafter, iron filterabilities dropped to below 30% and turbidities ranged from 0.3-0.8 NTU. Dosages of 0-3.3 ppm SiO_2 resulted in iron filterabilities of less than 30%and turbidities ranging form 0.87-1.3 NTU. The pH of the samples were controlled at either pH 7.0 or 8.0 (figure 20).

Practice Field Test At Ranielle, W. Va.

The second phase of this study was to develop detailed, quantitative documentation of effectiveness of sequestering in actual systems and to compare field tests with laboratory tests for similarity. The first step was a practice run performed in the small mining town of Ranielle which is located in the southern mountains of West Virginia. From this test, a procedure for collecting and analyzing samples was established. Well #6 was drilled to a depth of 200 ft into a hard, fine grained, slightly calcareous sandstone aquifer and the pumpage rate was 730 gpm. The 1985 analysis by the W. Va. State Health Dept. showed that iron and manganese were at concentrations of 0.58 and 0.08 mg/l, respectively (figure 21). Our analysis revealed that a rise in iron and manganese concentrations to 1.26 and 0.11 ppm, respectively had occurred. Hardness and alkalinity were consistent with the 1985 analysis (Table 6). Sodium silicate was injected at the well head but chlorine was not

Table 5. Five-day results of test 4 in which approximately 2 ppm iron was treated in the presence of 155-157 ppm as CaCO3.[a]

Sample [b]	SiO2 (ppm)	Day 0 Filterable Iron (%)	Day 0 Total Iron (ppm)	Day 0 Turbidity (NTU)	Day 0 pH [c]	Day 1 Filterable Iron (%)	Day 1 Total Iron (ppm)	Day 1 Turbidity (NTU)	Day 1 pH	Day 3 Filterable Iron (%)	Day 3 Total Iron (ppm)	Day 3 Turbidity (NTU)	Day 3 pH	Day 5 Filterable Iron (%)	Day 5 Total Iron (ppm)	Day 5 Turbidity (NTU)	Day 5 pH
10	0.0	15	2.12	1.3	7.0	23	2.06	1.2	7.3	12	2.04	1.2	7.2	31	2.04	1.2	7.4
11	3.3	27	2.11	0.87	8.0	14	2.09	1.0	8.0	5	2.09	1.0	8.0	12	2.09	0.91	8.1
12	10.5	97	2.12	0.29	7.0	4	2.10	0.62	7.2	1	2.09	0.58	7.3	4	2.09	0.54	7.2
13	9.8	97	2.12	0.33	8.0	5	2.11	0.78	8.0	2	2.09	0.72	7.9	5	2.09	0.63	8.1
14	11.4	99	2.10	0.29	7.0	27	2.11	0.50	7.2	5	2.08	0.76	7.3	8	2.09	0.63	7.1
15	27.9	98	2.12	0.27	8.0	7	2.09	0.76	8.1	2	2.06	0.62	8.0	2	2.08	0.51	7.8
16	24.6	98	2.12	0.27	7.0	98	2.10	0.33	7.3	3	2.09	0.53	7.2	4	2.06	0.42	6.7
17	33.4	99	2.12	0.28	8.0	98	2.09	0.35	7.6	4	2.09	0.63	8.2	3	2.04	0.51	7.5
18	37.6	99	2.12	0.32	7.0	98	2.11	0.31	7.1	96	2.10	0.27	7.4	92	2.12	0.26	7.3

Alkalinity = 160 ppm as CaCO3 to the methyl orange end point.

[a] Calcium chloride was added to the 22-L carboy to get 155- 157 ppm as CaCO3.

[b] All samples were greater than 91% ferrous iron.

[c] The pH of samples 10, 12, 14, 16, and 18 were adjusted to 7.0 while samples 11, 13, 15, and 17 were adjusted to 8.0 on each sampling day.

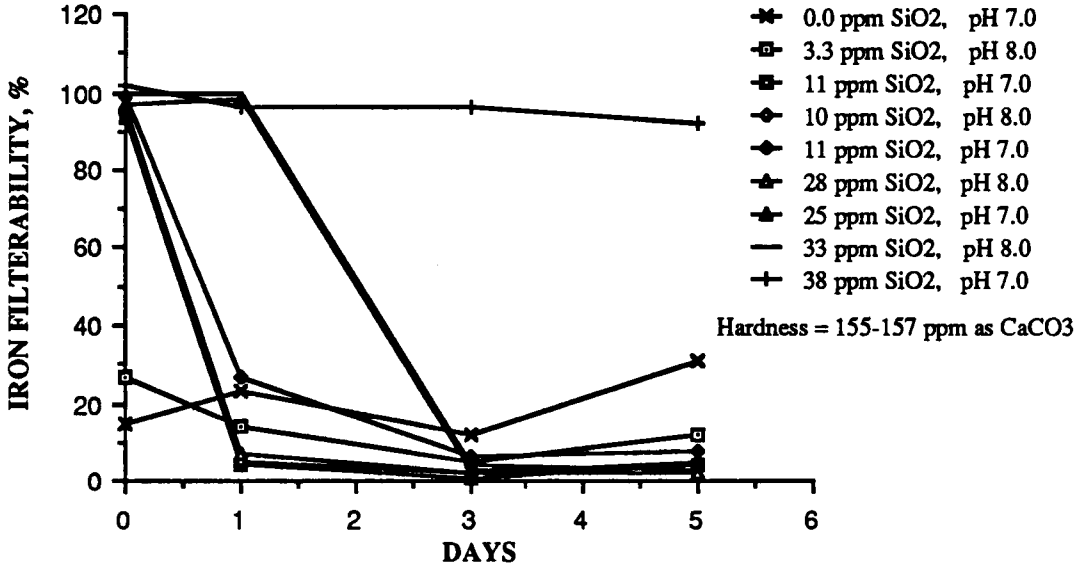


Figure 17. Filterable iron of samples from Test 4.

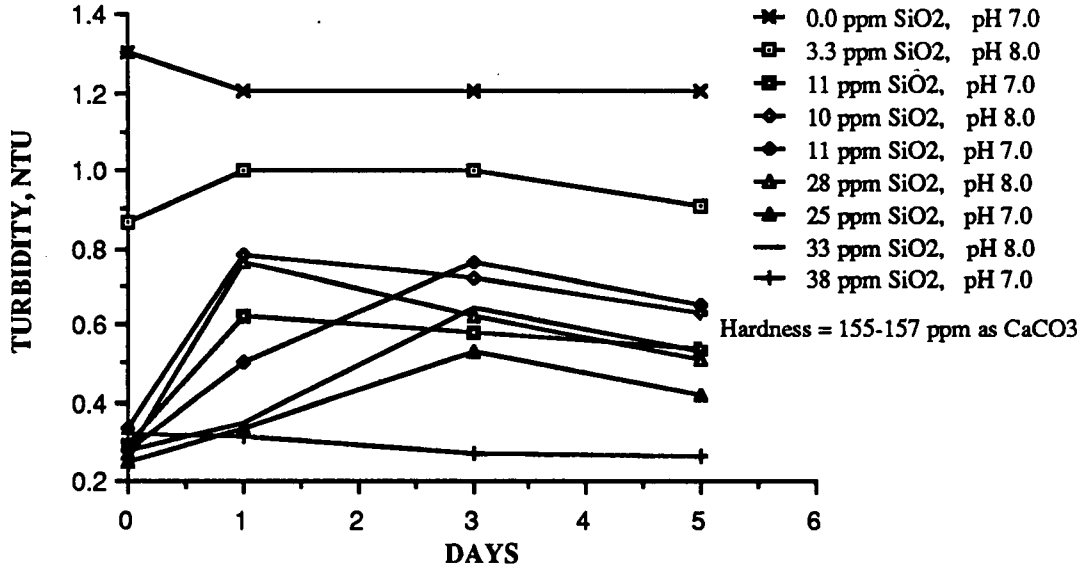


Figure 18. Turbidity of samples from Test 4.

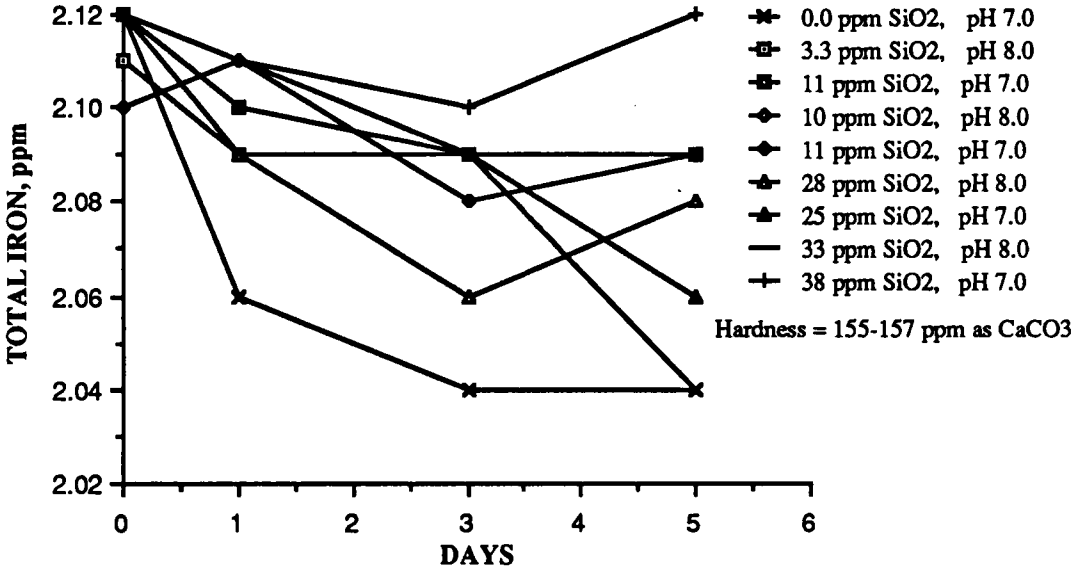


Figure 19. Total iron concentration of samples from Test 4.

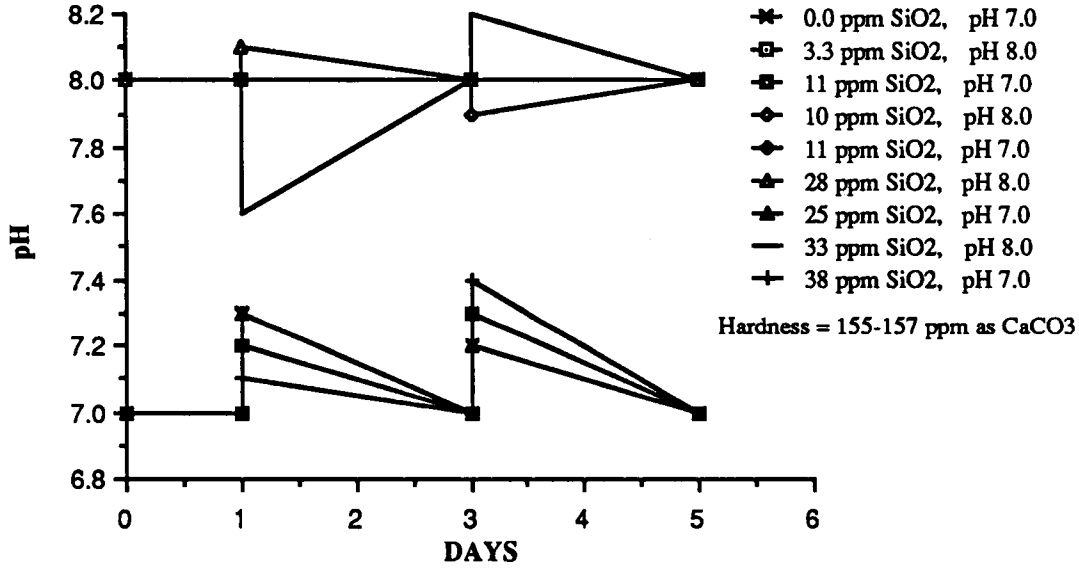


Figure 20. pH of samples from Test 4.

Ranielle Water Department

Point of Collection: Plant before coming into filter

Source: Raw water from well #6

Primary Contaminants (mg/l)[1]		Secondary Standards (mg/l)	
Arsenic (0.05)	0.00	Chloride (250.0)	10.0
Barium (1.0)	0.00	Copper (1.0)	0.0
Cadmium (0.01)	0.00	Iron (0.3)	0.58
Chromium (0.05)	0.00	Manganese (0.05)	0.08
Lead (0.05)	0.00	Sulfate (250.0)	0.0
Mercury (0.002)	< 0.0002	TDS (500.0)	174.0
Fluoride (1.0 optimum)	0.42	Zinc (5.0)	0.0
Turbidity (1.0 NTU)	1.1	Hydrogen Sulfide (0.05)	0.01
Selenium (0.01)	0.0	Methylene Blue Active	0.0
Silver (0.05)	0.0	Substance (foaming agents)	
Nitrate (as N) (10)	0.04	(0.5)	

Miscellaneous Parameters (mg/l)

Alkalinity (PHTH) (As $CaCO_3$)	0.0	pH (units)	7.8
Alkalinity (M.O.) (As $CaCO_3$)	159.0	Sodium	47.0
Hardness (As $CaCO_3$)	78.0		

[1] Maximum contaminant levels shown in parenthesis

Figure 21. 1985 Ranielle Water Analysis Report Source: West Virginia State Health Department.

Table 6. Five-day results from Ranielle, W. Va. iron stabilization field test in the presence of calcium and magnesium.[a] [b]

Sample [c]	Day 0							Day 1							Day 3							Day 5						
	Filterable Iron (%)	Total Iron (ppm)	Turbidity (FTU)	pH [d]	Color [e]	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)
10	97	1.26	10	7.6	-	109	0.11	20	1.38	7.7	7.3	80	108	0.12	12	1.31	7.1	8.0	67	100	0.11	13	1.04	5.7	8.3	37	100	0.10
11	104	1.17	2	7.0	10	100	0.11	16	1.17	3.0	7.3	58	100	0.12	8	1.16	2.8	7.9	59	100	0.11	11	1.04	2.6	8.4	17	100	0.10
12	104	1.17	2	7.0	10	100	0.11	30	1.22	1.8	7.3	63	100	0.13	7	1.14	1.7	8.5	58	75	0.12	13	1.16	1.8	8.4	18	55	0.11
13	104	1.17	2	7.0	10	100	0.11	14	1.25	2.6	7.7	55	100	0.12	6	1.20	2.6	7.2	58	100	0.11	9	0.96	2.1	7.5	9	91	0.11
14	97	0.92	10	7.2	100	100	0.12	13	0.91	0.79	7.5	47	69	0.13	7	0.89	0.84	7.8	57	62	0.13	7	0.92	0.88	8.4	4	58	0.12
15	108	0.78	5	7.3	100	83	0.12	54	0.78	0.76	7.6	44	80	0.10	4	0.78	0.77	8.2	37	60	0.10	11	0.81	0.81	8.5	2	56	0.09

Alkalinity averaged 170 ppm as CaCO3 to the methyl orange end point. Alkalinity dropped to 164 ppm in the distribution mains.

[a] Sample 10 is the raw sample which had 11 ppm as SiO2 naturally occurring. All other samples were treated with approximately 4 ppm as SiO2.

[b] Hardness totaled approximately 73 ppm as CaCO3 in the raw sample. Magnesium contributed 46 ppm as CaCO3.

[c] All samples were below 70% ferrous iron. There was a 30 minute delay before acidification of samples.

[d] The pH of sample 13 was adjusted to 7.0 on each sampling day.

[e] Color is apparent color units.

added until the treated water had reached the chlorination basin. The Ranielle Water Dept. was filtering the water between silicate addition and chlorination which was unusual and probably would not give the best results since the silicate could depolymerize before the chlorine oxidizes the iron. Therefore this was considered only as a practise test. As of last report, the sodium silicate was off-line and only filtration was occurring (probably still before chlorination).

Iron stabilization was only occurring for less than one day at Ranielle. Apparently most of the iron was passing through the filters and then oxidized during chlorination if aeration had not already occurred. Approximately 100% iron filterability occurred at day 0, but dropped to 54% or below on day 1 (figure 22). Turbidities were extremely high ranging form 0.8 to 3.0 NTU for all treated samples (figure 23). The high turbidities of the distribution samples on day 0 were suspect due to fluctuations in the Hach field kit which was later corrected. The pH of all the samples was allowed to drift except for one in which it was controlled at pH 7.0 (figure 24). Even though poor treatment was occurring, the total iron concentration stayed relatively constant (figure 25) which usually indicates that stabilization is occurring. The apparent color of the raw and treated waters were originally very high and decreased over the test period (figure 26). The EPA Secondary Drinking Water Regulations limit color to 15 color units [42]. The samples were not filtered before color was determined.

Manganese stabilization lasted up to five days for the untreated, treated, and treated pH-controlled samples from the plant, but only three days of stabilization occurred with the high temperature and distribution samples (figure 27). As with total iron, total manganese was relatively constant (figure 28).

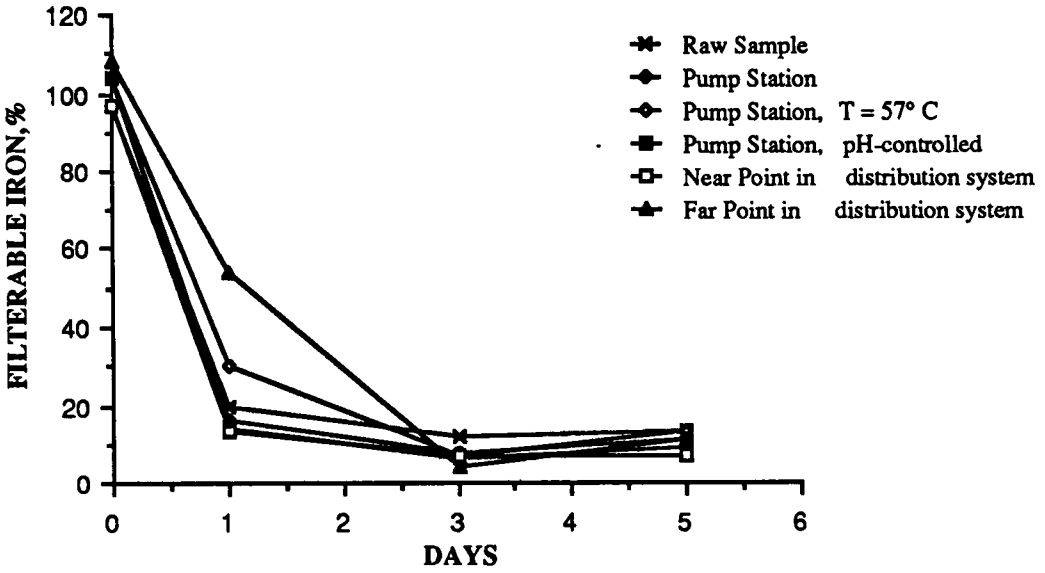


Figure 22. Filterable iron samples from Ranielle, W. Va.

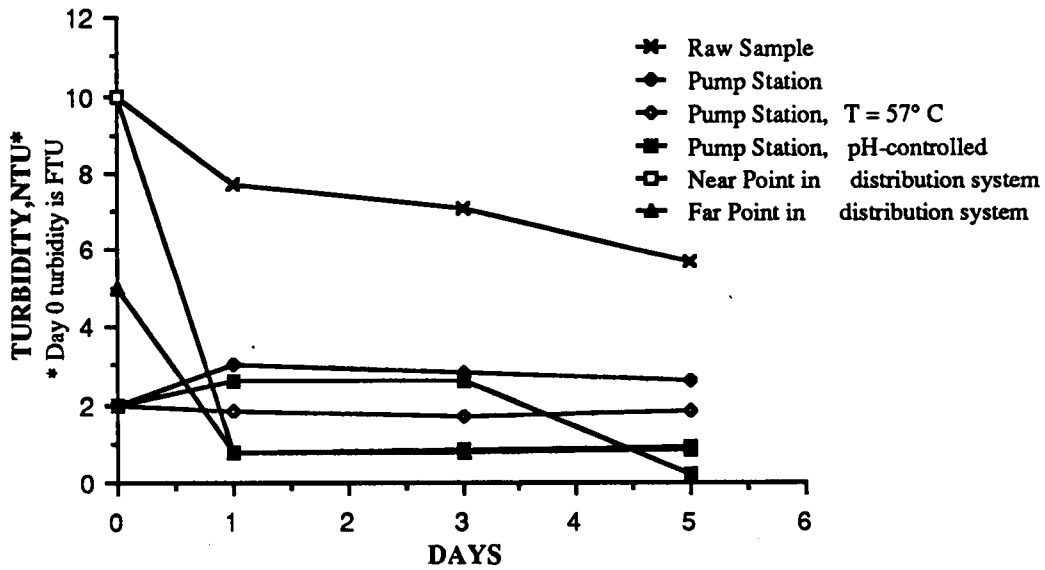


Figure 23. Turbidity of samples from Ranielle, W. Va.

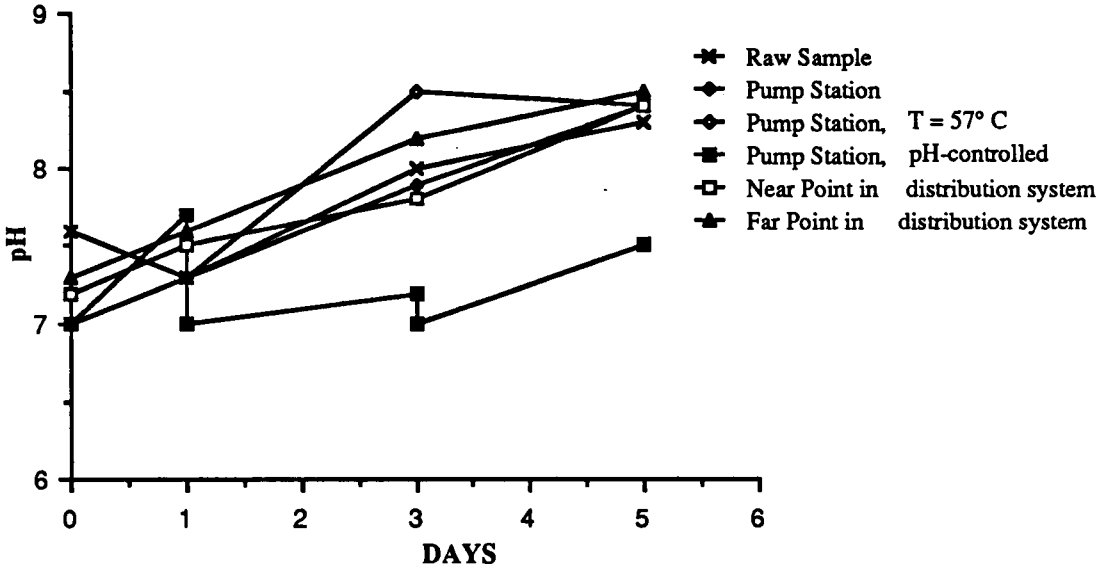


Figure 24. pH of samples from Ranielle, W. Va.

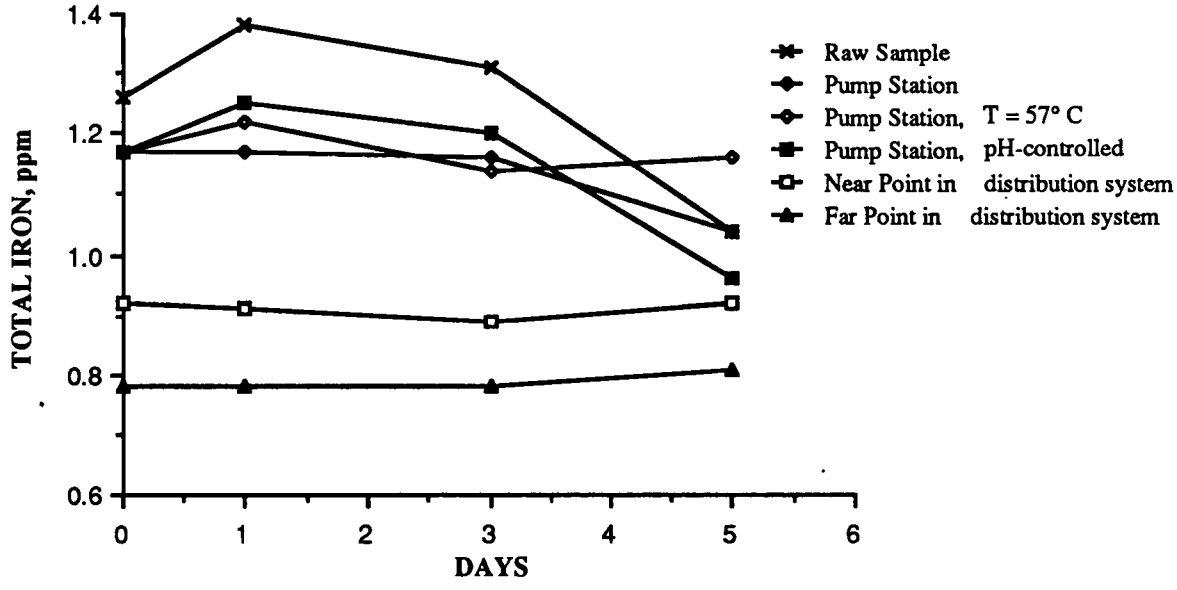


Figure 25. Total iron concentrations of samples from Ranielle, W. Va.

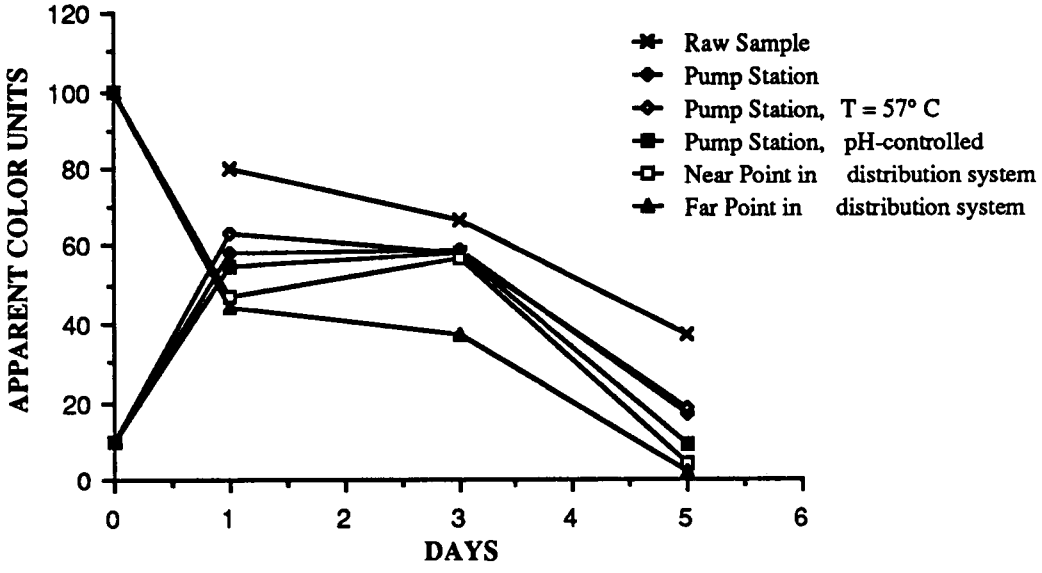


Figure 26. Apparent color of samples from Ranielle W. Va.

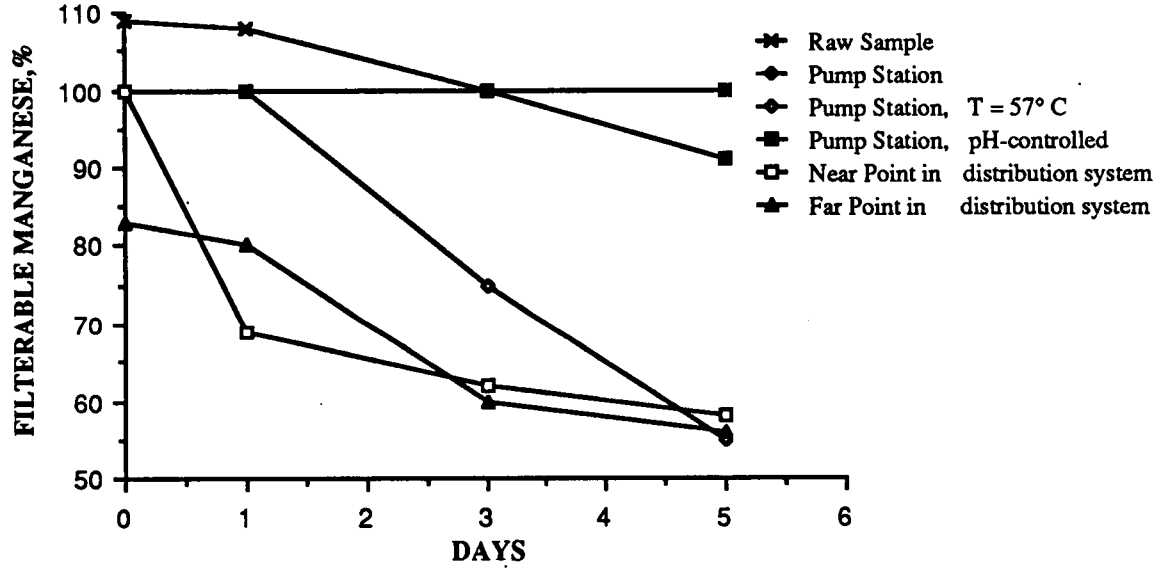


Figure 27. Filterable manganese from Ranielle, W. Va.

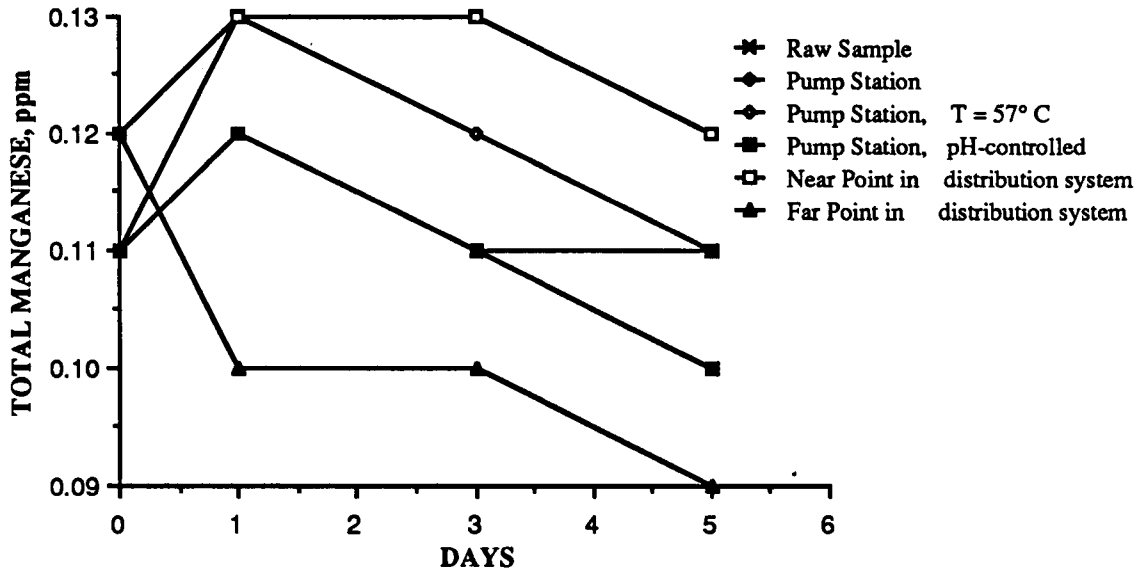


Figure 28. Total manganese concentrations of samples from Ranielle, W.Va.

Wisconsin Field Studies

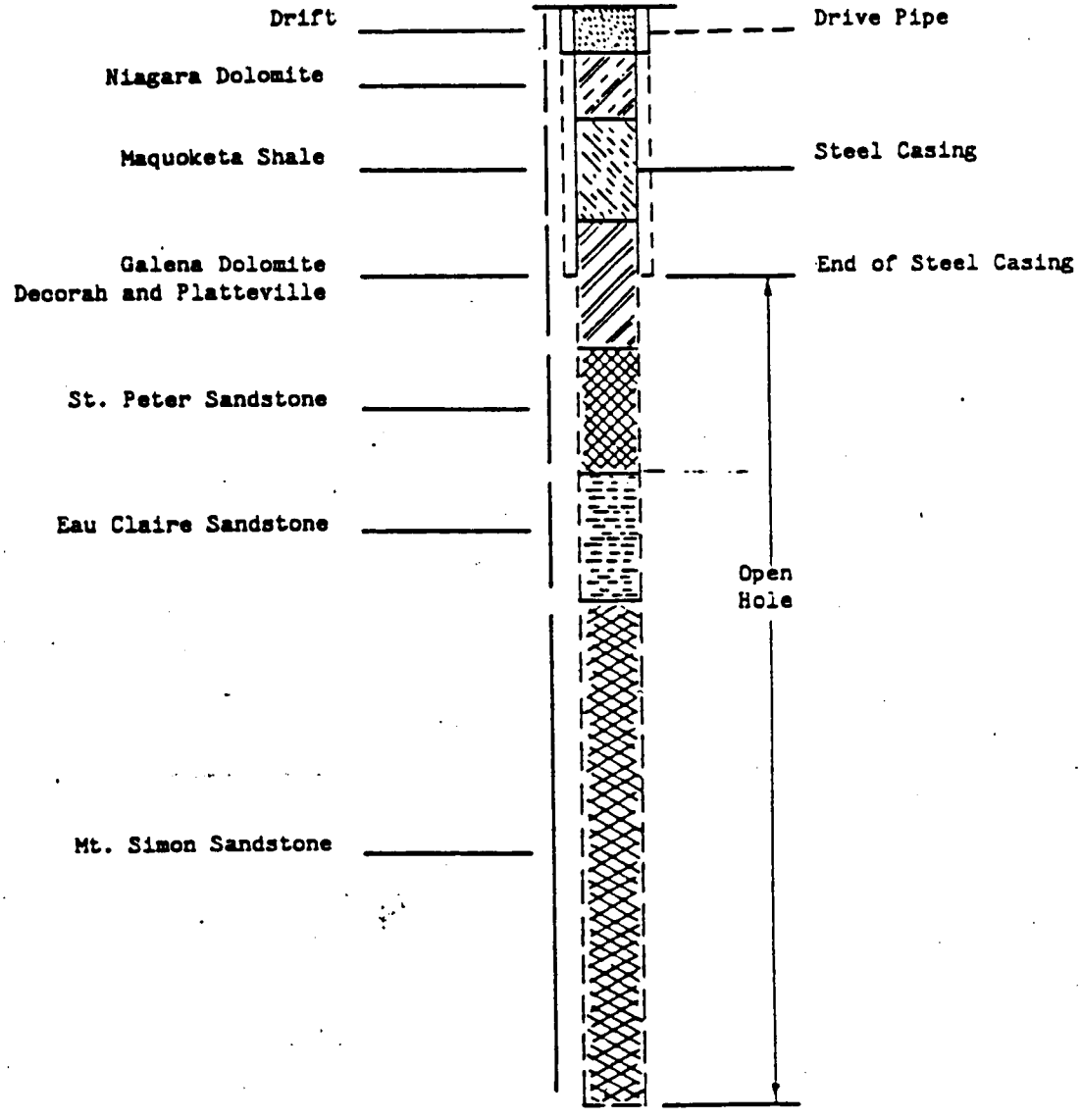
Case History of Waukesha [43]

The Waukesha Water Utility is currently supplying a population greater than 50,000 from 10 high capacity deep wells. The wells average 16" in diameter and are approximately 2040' deep terminating in a sandstone aquifer (Figure 29). The average groundwater level is approximately 417 feet from the surface. The average capacity of the wells is 1,229 gpm and the average consumption is 240 gpd for a family of four.

A red water problem developed in the early 1970's due to iron in the groundwater which ranged from 0.12. 0.58 mg/l. The groundwater at the time was chlorinated and fluoridated at the well. Chlorination, along with exposure to oxygen, was precipitating and depositing the natural iron in the distribution system causing the red water problem. Contribution of iron from the 212.7 miles of ductile, cast iron water mains was deemed

TYPICAL WELL LOG

IN WAUKESHA AREA



Depth: 1,835' to 2,266'
Diameter: 12" to 27"

Figure 29. Waukesha well data.

insignificant. Several treatment schemes were tried, including flushing the system twice a year, but all fell short of correcting the problem of red water. Due to the distance between wells, it was unfeasible to build a single treatment plant and the use of pressure filters at each well was prohibitive due to economics and space limitations. Therefore, a sequestration method was chosen to control the red water problem.

From laboratory tests, Waukesha developed a feed rate equation for determining the amount of sodium silicate needed to stabilize 73% of the naturally occurring iron (The percentage of iron stabilized is the percentage of iron passing through a paper filter, although Waukesha actually measures the iron captured on the filter.),

$$\text{Feed rate} = (8.34\ Q\ C\ SF)/(R\ D\ 10^6)\ \text{gal/ hr} \qquad (47)$$

Q = flow (gal/hr)
C = SiO_2 concentration (mg/l)
D = density of solution (lb/gal)
SF= safety factor of 1.8
R = percentage of SiO_2 in the sodium silicate solution

The feed rate is further adjusted until the unstable iron concentration is 0.10 mg/l, i. e. iron captured on a filter is 0.1 mg/l. Polyphosphates were also tested but reportedly stabilized a lower percentage of iron than the same concentration of silicate solutions.

A 10-day pilot test using N® silicate with a weight ratio of 3.22 SiO_2/Na_2O and approximately 28% SiO_2 was conducted at well no. 8. A positive displacement feed pump was synchronized with the well pump operation and the sodium silicate was injected after the chlorine injection point (Figure 30). The pilot test needed a 52% higher SiO_2 concentration to obtain 73% stabilization of the iron than indicated by laboratory tests.
The 1974 cost estimate was an initial cost of $12,200 for installation and equipment. The estimated annual cost of operation was $17,860. This converts to a per

WAUKESHA WATER UTILITY
SODIUM SILICATE APPLICATION SYSTEM
(TYPICAL)

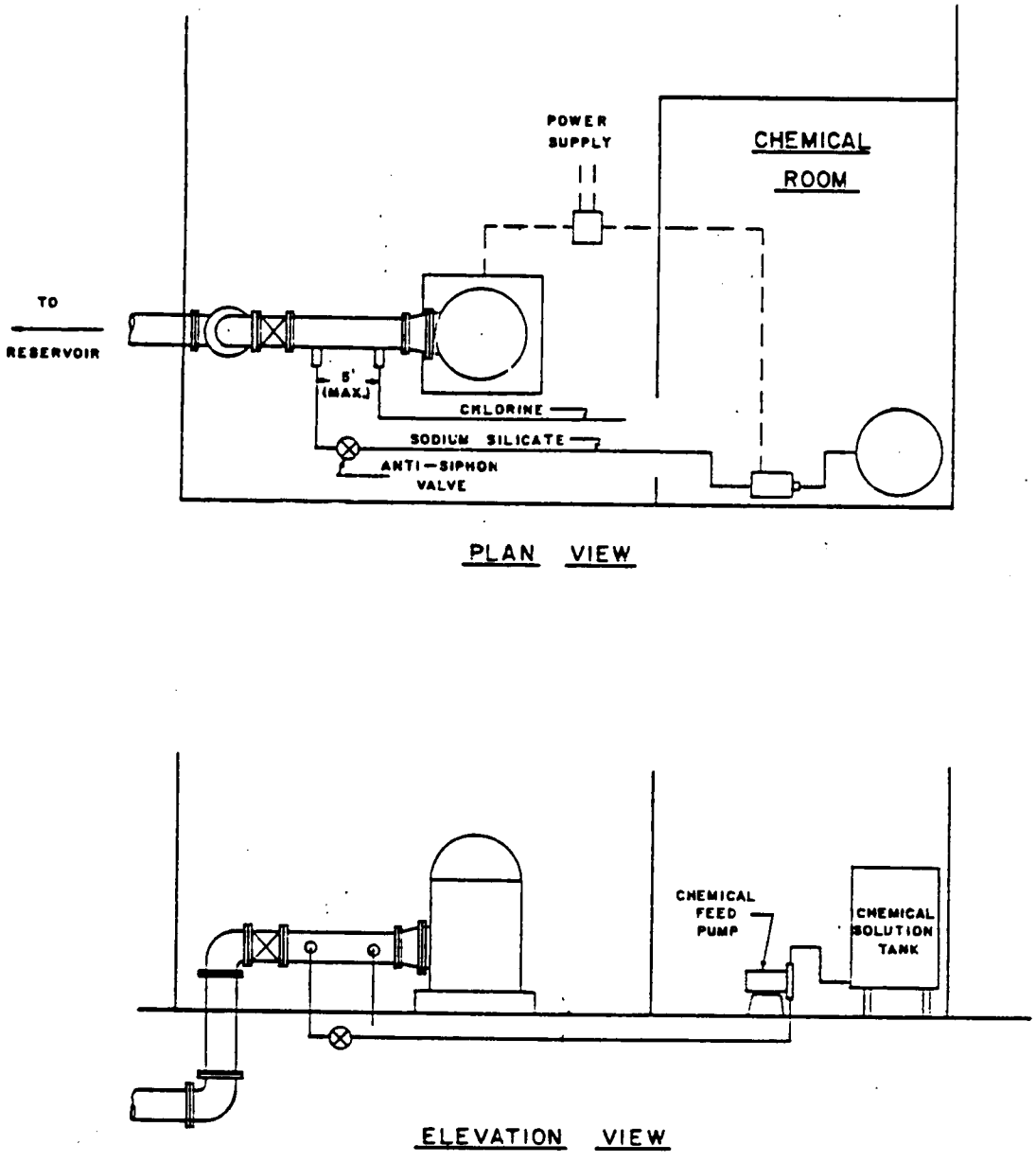


Figure 30. Diagram of typical sodium silicate application at Waukesha.

capita cost of $0.34/person/year. The sodium silicate. chlorine treatment was initiated in January of 1975.

Results of Waukesha Field Study

The field study was conducted at the Wolf Rd. pump site (well 10). At the site, N. silicate is injected into a 12" diameter pipe 8" downstream from the chlorine injection point, at a calculated average feed rate of 20.99 mg/l which is 6.02 mg/l as SiO_2 (about 6.84 mg/l as SiO_2 by our measurement [Table 7]). An average of 73.5% of the iron (measured at 0.3 mg/l) is successfully stabilized. The capacity of the pump is 2236 gpm and supplies 31.1% of Waukesha's water use. A chemical analysis of the water is provided in figure 31.

Analysis of the field samples collected after silicate addition and studied for several days show that the filterability of the iron drops after Day 1 (Figure 32), which means that the iron is becoming unstable. Earlier laboratory tests have shown that 12 ppm SiO_2 can hold or sequester 2 ppm Fe for 3 to 5 days in the absence of calcium. The reduction in treatment after Day 1 at Waukesha should be due to several phenomena observed previously. Earlier laboratory tests have shown that iron stabilization will decrease over time and that higher levels of divalent ions, calcium and probably magnesium, will reduce treatment effectiveness. Also, higher levels of silicate will lengthen the time of effective treatment. All of these observations should apply in this case.

The drop in filterability with time for the above samples also correlates with the low filterability of samples from the distribution system. Water is pumped from the wells to the reservoirs with a detention time of 1/2-1 day. After water enters the distribution system, iron stability is less than that initially at the well. Some complaints of red water have been reported after a detention time of one day in the reservoirs, but no complaints are received when the detention time is 1/2 day.

Table 7. Five-day results from Waukesha iron stabilization field test[a] in the presence of calcium and magnesium.[b]

Sample[c]	Day 0					Day 1					Day 3							Day 5				
	Filterable Iron (%)	Total Iron (ppm)	Turbidity (FTU)	pH[d]	Color[e]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color
10	23	0.30	3.0	7.2	28	48	0.25	1.1	7.5	12	42	0.19	1.0	7.7	9	105	0.082	46	0.13	0.78	7.8	5
11	88	0.24	3.0	7.2	14	100	0.24	0.16	7.6	12	32	0.22	0.25	7.8	11	72	0.079	26	0.19	0.21	7.9	3
12	88	0.24	3.0	7.2	14	100	0.24	0.16	7.6	12	83	0.23	0.26	7.5	33	104	0.071	35	0.20	0.26	7.8	13
13	88	0.24	3.0	7.2	14	22	0.23	0.22	7.6	8	28	0.22	0.24	7.0	18	66	0.077	11	0.18	0.21	7.3	8
14	28	0.50	1.0	7.2	13	58	0.48	1.0	7.6	9	41	0.49	1.0	7.8	7	52	0.113	2	0.49	0.98	7.9	16
15	46	0.13	2.0	7.2	27	57	0.14	0.44	7.7	7	64	0.14	0.42	7.9	5	73	0.059	59	0.17	0.36	8.0	0

Alkalinity = 169 ppm as CaCO3 to the methyl orange end point.

[a] Sample 10 is the raw sample which had 7.8 ppm as SiO2 naturally occurring. All other samples were treated with approximately 6.8 ppm as SiO2.

[b] Hardness totaled approximately 250 ppm as CaCO3. Magnesium contributed 97 ppm as CaCO3.

[c] Sample 10 had 70% ferrous iron. All other samples were 50% or less. Some aeration did occurr during sampling.

[d] The pH of all sample 13 was adjusted to 7.0 on each sampling day.

[e] Color is apparant color units.

Chemical Analysis of Waukesha Water

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
Alkalinity (as $CaCO_3$)	214	Manganese	0.07
Calcium	73	Nitrates (as N)	< 0.5
Chlorides	8	Sodium	12
Fluorides	0.5	Sulfates	116
Hardness	290	Total Solids	442
Iron	0.20	pH (units)	8.0
Magnesium	26	Silica (reactive)	.

Figure 31. Raw water analysis at Wolf Rd Well #10.

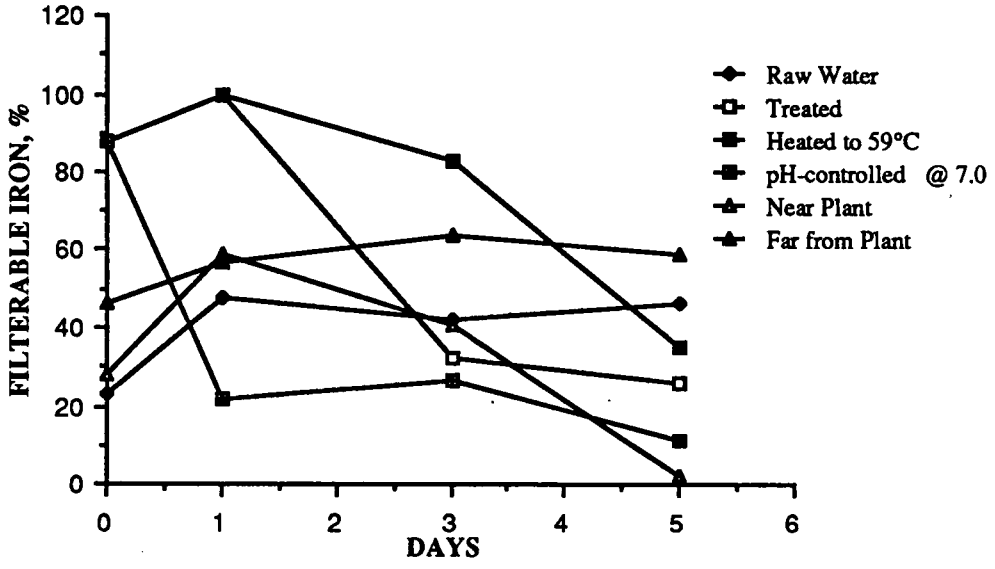


Figure 32. Filterable Iron samples from Waukesha, Wisc.

These results correlate with previous laboratory tests. As stated earlier, 12 ppm SiO_2 sequesters 2 ppm Fe. Under the same conditions and in the presence of 50 ppm of $CaCO_3$, successful sequestration drops down to only one day.

Unfortunately only complete manganese data are available for Day 3. Results show that the manganese filterability is higher than the iron filterability. Also, the untreated raw water has 100% filterability, indicating no treatment, though impractical, is better than treating the manganese with sodium silicate and chlorine. This is consistent with laboratory results reported by Robinson and Ronk (38).

Two other parameters, pH and temperature were also studied in this test. One sample was maintained at pH 7.0 while the another was maintained at a temperature of 59° C from Day 1 to Day 5. Figure 32 shows that a pH 7.0 solution has less filterability, i.e. less treatment effectiveness, than solutions of uncontrolled pH in which the pH rose to about 8.0 (figure 33). Turbidity for the controlled pH sample was approximately 2.5-5 times higher than the uncontrolled pH samples (figure 34). This correlates with earlier work by Browman in which lower pH values were less effective in treatment. Manganese filterability is slightly lower at pH 7.0 on Day 3 which also indicates less effective treatment at a lower pH. Figure 28 also indicates that at higher water temperatures, iron filterability is greater than filterability at lower temperatures. Day 3 manganese filterability is also in agreement with 100% filterability compared to 70% filterability at lower temperatures. These results conflict with visual sighting of precipitates in the high temperature sample but no visual sighting of precipitates in the low temperature samples. The turbidities were comparable for heated vs non-heated samples, but the color is significantly higher for heated sample (figure 35). Turbidity was high on Day 0 due to air bubbles in the samples and probably should be ignored.

Currently the only complaints of red water are related to system disturbances, such as pump switching and flushing. Other phenomena include silicate deposits in meters due to

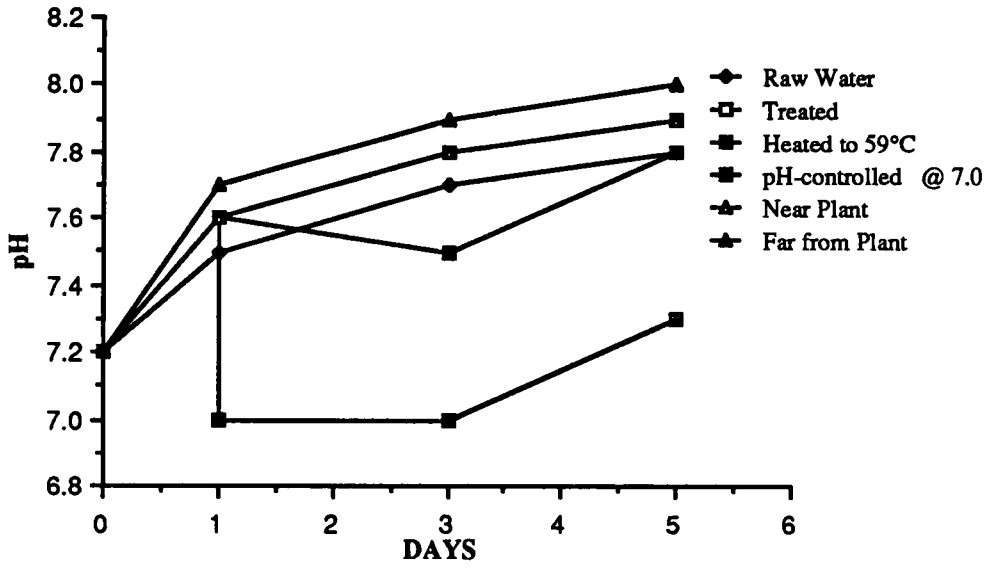


Figure 33. pH of samples from Waukesha, Wisc.

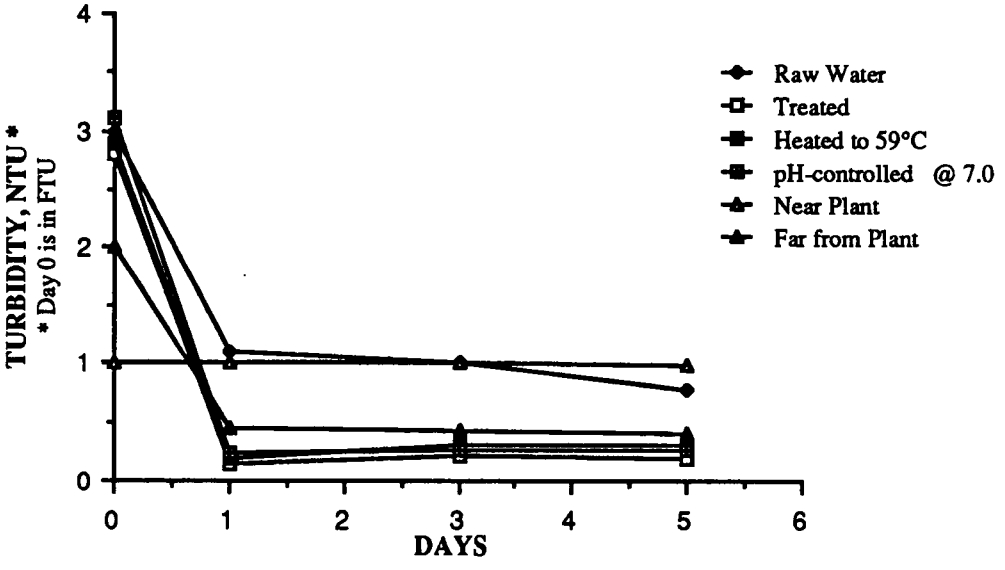


Figure 34. Turbidity of samples from Wauksha, Wisc.

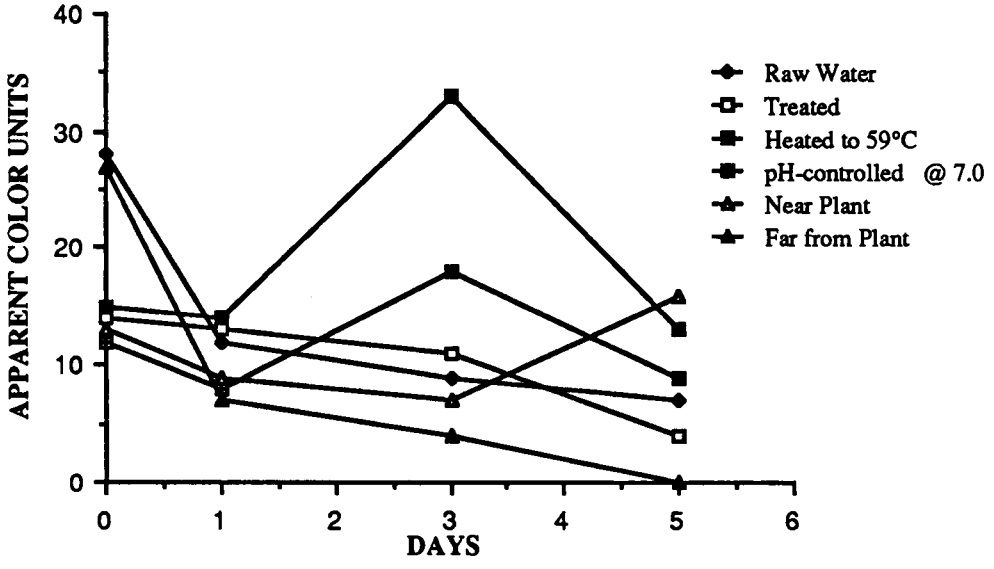


Figure 35. Apparent color of samples from Wauksha, Wisc.

silica feed. Deposits are found in the meters, which the utility believes are due to silica and some of the workers believe a sludge is being added to the water. The iron oxide deposits and have increased the efficiency of the meters since the induction of silicate into the system. Occasionally, excess silicate build-up will clog the meters. The Waukesha Water Utility has no evidence that silica is a constituent of the deposits but an increase in the amount of the deposits occurred after the sodium silicate went on-line.

Case History of Butler [45]

The Butler Water Utility is much smaller than the Waukesha Utility servicing approximately 2000 people. One well was drilled in 1966 through a similar lithology as the Waukesha terminating in a sandstone unit. Groundwater is pumped into a 400,000 gallon ground storage tank then to a 300,000 gallon elevated reservoir before entering the

distribution system. Fluoridation and chlorination began in 1968 using a 25% hydrofluorosilicic acid solution and a 15% calcium hypochlorite solution. In 1973, polyphosphate (Aquadene) was added to treat the iron problem.

Many attempts, including polyphosphate, were unsuccessful in reducing the complaints of red water. Until 1973, the only effective measure was to increase the flushing of the system and periodically drain the ground storage tank and remove accumulated iron deposits. Later in 1973, a sodium silicate. sodium hypochlorite treatment scheme was successfully incorporated to reduce the red water problem.

Investigations by Bionomics Corps revealed that in the first 10-30 minutes of pumping, iron and sulfide concentrations were higher, indicating a multiple aquifer system. After the first ten minutes of pumping, the iron concentration is three times higher than after twenty minutes of pumping. Prior to the silicate method of sequestering, chlorine oxidized all the iron to an insoluble iron oxide at the well head. Due to the high iron concentration during the well start-up time, no chlorine residual could be found in the distribution system until the iron level dropped. Also some precipitated iron passed into the distribution system during the start-up time.

To treat the red water problem, Butler currently adds chlorine as a 15% solution of sodium hypochlorite and, one foot after the chlorine injection point, injects sodium silicate as an N-silicate solution at 5 ppm SiO_2 to get 12 ppm SiO_2 when the natural occurring silica is included. Six days after first starting silicate treatment, iron was in a soluble form in the treated water leaving the pump station. (Here "soluble" means that the iron did not show significant color or turbidity, but the iron could be in a colloidal form.) After two weeks, soluble iron was maintained in the storage tank, but the distribution system contained iron oxides. Iron was stabilized in the distribution system near the well after three months of treatment and 40-60% of the unstable iron particles were less than 8μm in size. After 300 days, the most difficult section of the distribution system showed

successful treatment through a 0.45μm filter, and, one year after treatment, complaints dropped to near zero.

During the study period, the use of 8μm filters for samples in the distribution system gave higher filterabilities than the usage of 0.45μm filters. With the 0.45μm filters, no change in the effectiveness of treatment could be noted, but visual reports of the water indicated the sodium silicate treatment was working. Therefore the filter pore size was increased to 8μm. Also no complaints by customers were recorded when iron colloids passed through the 8μm filter. Colloidal iron-containing particles were apparently greater than 0.45μm in size but below the visual limit of 40 μm in size. Therefore, the 8μm filter was deemed safe for the standard filter for determining treatment efficiency in the distribution system. (In previous work at UT, poor filterability through a 0.1 μm filter generally correlated with high turbidity and high filterability with low turbidity when treating 2 mg/l of iron. Butler's lower iron level of 0.4 mg/l may cause turbidity to be relatively insensitive to treatment effectiveness and allow 8 μm filters to be satisfactory.)

Since the introduction of the sodium silicate treatment, a reduction in costs and complaints has occurred. Operational costs have dropped due to the reduction in chemical and mechanical cleaning costs. The only complaints have been red water from the hot water tap, which were corrected by flushing the water heater.

Results of Butler Field Study

Results from the field study (table 8) show that iron filterability of treated water on Day 0 is approximately 70%. On Day 1 iron filterability drops to below 20% through the 0.1μm filter (figure 36), but total iron concentrations were relatively constant (figure 37) which was inconsistent with lab results where a drop in filterability was accompanied with unstable total iron concentrations. Curiously by Day 5, the raw water filterability is highest at 27%,albeit still low. Manganese filterability on Day 3 is 100% for the raw water and

Table 8. Five-day results from Butler iron stabilization[a] field test in the presence of calcium and magnesium.[b]

Sample[c]	Day 0					Day 1					Day 3							Day 5				
	Filterable Iron (%)	Total Iron (ppm)	Turbidity (FTU)	pH[d]	Color[e]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color
16	19	0.43	2.0	7.3	6	4	0.45	3.5	7.6	22	21	0.34	3.1	7.7	15	105	0.065	26	0.23	1.9	7.9	8
17	70	0.43	1.0	7.3	-	5	0.41	0.37	7.7	4	13	0.38	0.37	7.8	4	70	0.064	7	0.46	0.33	7.9	1
18	70	0.43	1.0	7.3	-	5	0.41	0.37	7.7	4	8	0.39	0.41	7.8	13	72	0.060	3	0.38	0.37	8.0	26
19	70	0.43	1.0	7.3	-	10	0.40	0.36	7.7	0	15	0.39	0.32	7.0	11	65	0.066	2	0.46	0.32	7.3	14
20	13	0.31	1.0	7.1	9	6	0.34	0.32	7.7	0	13	0.32	0.32	7.9	4	91	0.056	8	0.36	0.32	7.9	10
21	23	0.35	2.0	7.3	32	5	0.37	0.36	7.8	0	6	0.35	0.35	7.9	8	59	0.058	20	0.44	0.36	7.9	3
	Water Heater sample																					
20	13	0.08																				

Alkalinity = 144 ppm as CaCO3 to the methyl orange end point.

[a] Sample 16 is the raw sample which had 8.2 ppm as SiO2 naturally occurring. All other samples were treated with approximately 8 ppm as SiO2.

[b] Hardness totaled approximately 315 ppm as CaCO3. Magnesium contributed 85 ppm as CaCO3.

[c] Sample 16 had 94% ferrous iron. All others were at 33% or below.

[d] The pH of all sample 19 was adjusted to 7.0 on each sampling day.

[e] Color is apparant color units.

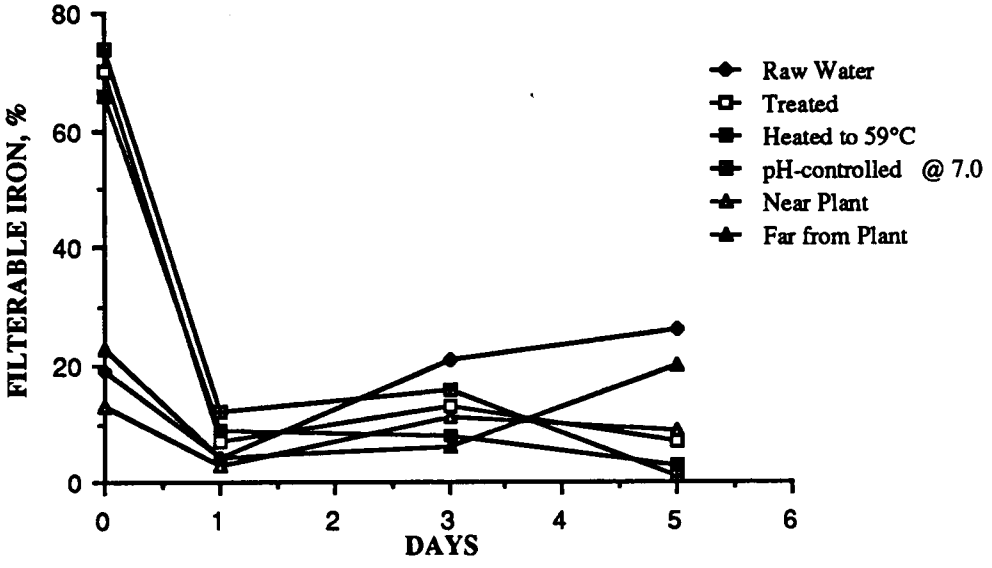


Figure 36. Filterable iron samples from Butler, Wisc.

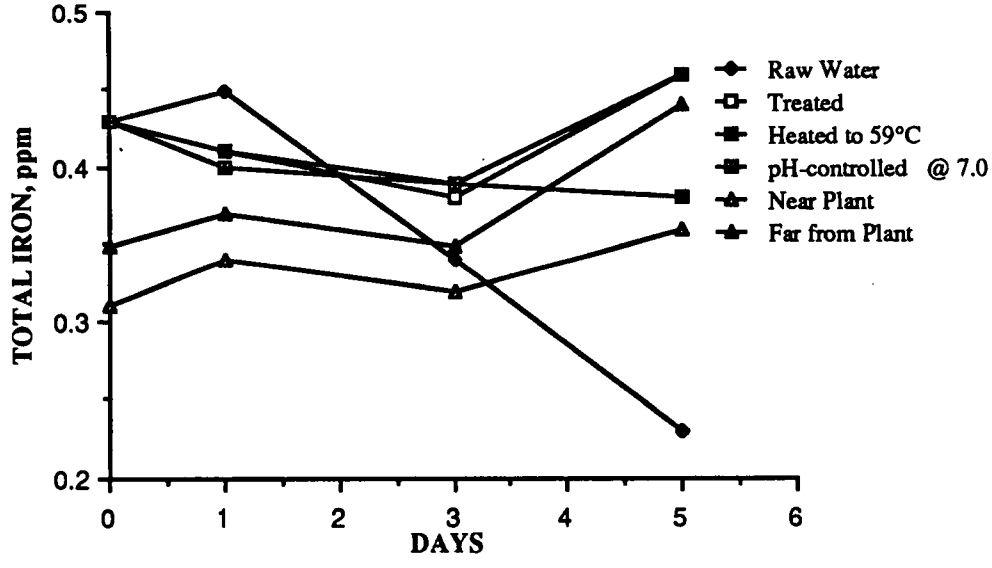


Figure 37. Total iron concentrations of samples from Butler, Wisc.

70% for the treated water. As with the Waukasha data, indications are that the manganese is better treated by no treatment. Over the five day period, turbidity ranged between 0.32-0.42 NTU (figure 38) and pH rose toward a value of 8.0 (figure 39).

The treated sample at pH 7.0 and the other at 59° C show no discernible difference in iron filterability when compared to the treated sample with unadjusted pH, which is in contrast to results at Waukesha. Visual inspection of the sample at 59°C revealed a visible precipitate and significantly higher color (figure 40) while the other treated samples contained no visible precipitate and lower color. Only 13% filterability occurred with the water heater sample.

In future field tests, it is recommended that filtration through either a 0.45μm or 8μm filter should be included in the filtration analysis. This will enable better comparisons with the water utility's records since they typically use these size filters as standards in their analysis of stabilized iron. Also repeating laboratory tests at lower iron concentrations than the previous 2 mg/l would be helpful for comparisons with field sites.

Ontario, Canada Field Studies

Case history of Oak Ridges [46]

The Oak Ridges's water system has three wells and one 1,000,000 imperial gallon standpipe which supplies a population of 5500. The lithology, into which the wells are drilled, is a mixture of clay, gravel, and sand, with a packed sand and gravel formation surrounding the well screen at a depth of 377 ft. This information along with other well data of the site can be found in the Appendix. The most current analysis, at the time of testing, of the raw and treated water quality is presented in figure 41. The high turbidity of the raw water may result from oxidation of the iron after sampling.

From 1978 to 1981, the treatment scheme of the Oak Ridges water supply has changed no less than eight times due to persistent iron-related complaints. Prior to 1978,

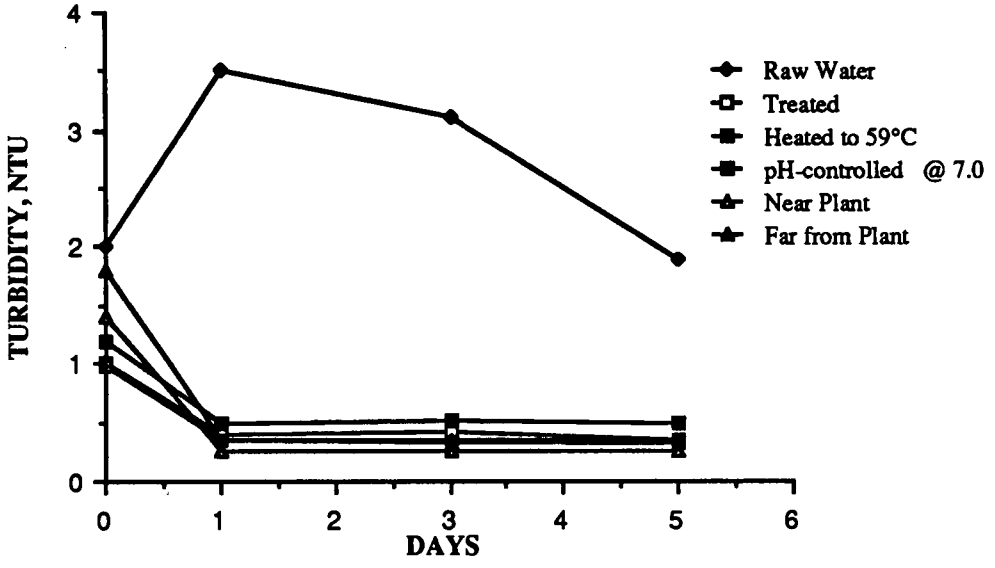


Figure 38. Turbidity of samples from Butler, Wisc.

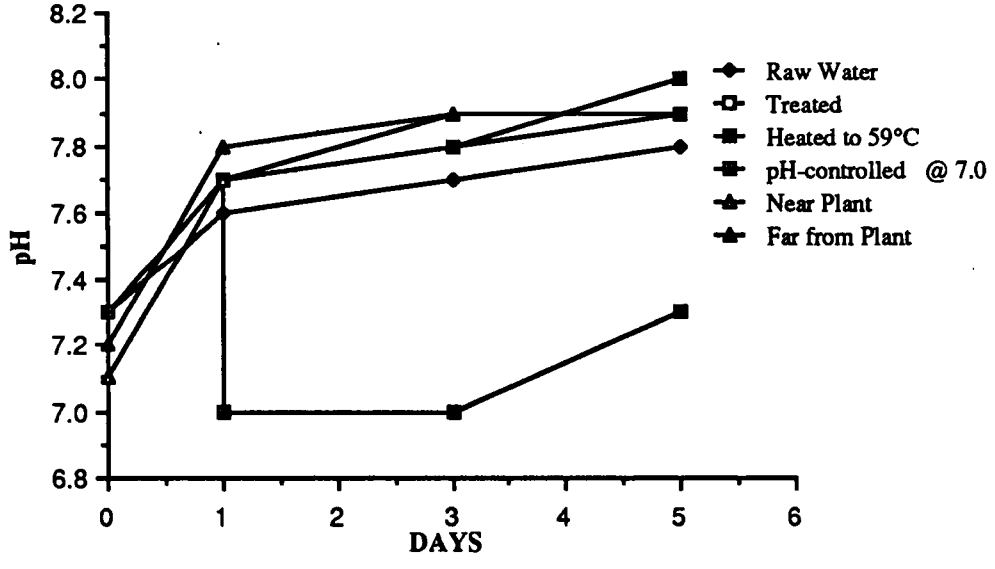


Figure 39. pH of samples from Butler, Wisc.

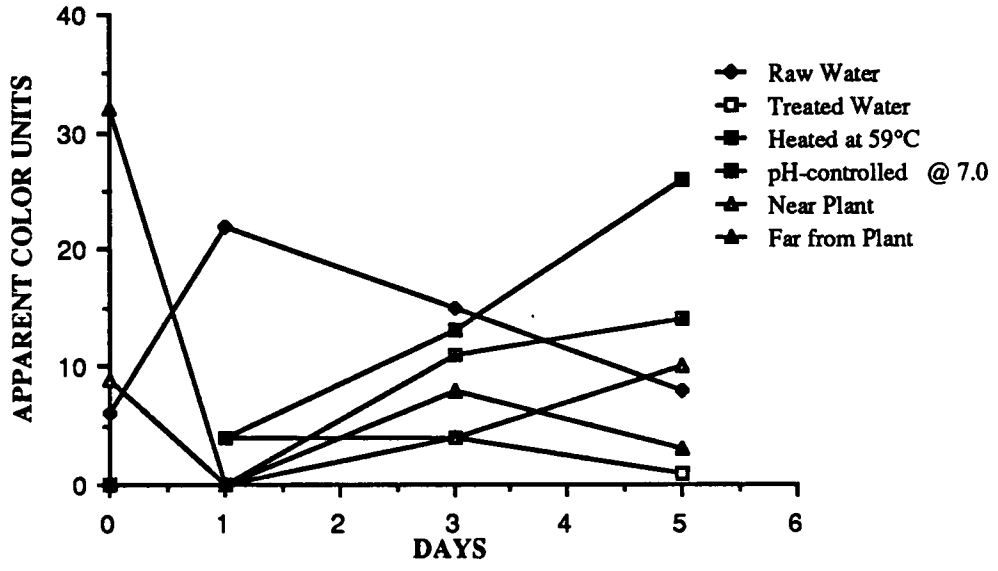


Figure 40. Apparent color of samples from Butler, Wisc.

	Total Raw	Total Treated
Iron, mg/l as Fe	1.5	1.5
Manganese, mg/l as Mn	0.030	0.030
Conductivity @ 25° C, UMHO/CM	489	499
Hardness, mg/l as $CaCO_3$	259	259
Alkalinity,mg/l as $CaCO_3$	256	257.9
pH	7.94	8.07
Fluoride, mg/l as F	0.10	0.10
Chloride, mg/l as Cl^-	1.65	4.65
Sulfate, mg/l as as SO_4	13.10	12.90
Nitrates, mg/l as N	0.10	0.10
Turbidity, FTU	16.10	0.65
True Color	11.0	2.5

Figure 41. Water quality of Oak Ridges conducted by the Ministry of Environment (M.O.E.) as of July 30, 1987.

the water was chlorinated with chlorine gas and filtered by a system of four pressure filters. In January of 1978 caustic soda and aluminum sulfate were added to the treatment scheme but complaints of dirty water were still common. After two months, the caustic soda and aluminum sulfate were shut off, the pressure filters were taken off-line, and sodium silicate was introduced during March. After almost two years of sodium silicate treatment, the pressure filters were put back on-line in February of 1980 and in March sodium hydroxide replaced the sodium silicate. Since this treatment scheme produced poor results, the sodium hydroxide was taken off-line in May of 1980 and then two months later the sodium silicate was back on-line, but was again taken off-line in December of 1981. On September 24, 1984, the pressure filters were finally taken off-line and converted to bulk storage containers for the sodium silicate. Finally, the best treatment scheme in which to minimize the number of iron-related complaints was a combination of chlorine oxidation at 3.0 to 4.0 mg/l and sodium silicate sequestration at 18 mg/l as SiO_2.

Currently, most red water complaints are mainly occurring at distant points along the distribution system, where York Engineering believe that chlorine residuals are too low to maintain iron sequestration. Future treatment plans are to implement additional chlorine treatment at the standpipe to ensure a higher chlorine residual at far sites to reduce the number of red water complaints.

Sampling Procedures at Oak Ridges

On day 0, six 2-L samples were taken at pre-determined sites. One raw sample and three treated samples were drawn from two taps in the pump station, which was pumping at 238 gpm (US). As a reference, figure 42 gives the monthly flows and the average pumpage rate for each pump as well as total consumption of chlorine and sodium silicate for 1987. A water hose was used for these samples to reduce the possibility of aeration during the drawing of the samples at the pump station. The Provincial Police Dept. was

1987 Monthly Flow (US gal)		Chlorine Gas (lb)	N-Sodium Silicate (US gal)
January -	14,458,750	450	625
February -	12,700,780	349	461
March -	14,853,700	435	642
April -	18,129,940	541	846
May -	22,862,140	637	832
June -	18,129,940	535	734
July -	19,644,240	506	703
August -	21,423,340	710	900
September -	16,388,330	546	730
October -	14,603,950	471	702
November -	13,484,330	438	604
December -	13,447,100	420	634
Totals -	**200,523,800**	**6,038**	**8,412**

Average 1987 Flow = 540,000 US gpd

No. 1 well flow = 270 gpm

No. 2 well flow = 510 gpm

No. 3 well flow = 510 gpm

Figure 42. Monthly flow and consumption of chlorine and sodium silicate, and average flow of each well at Oak Ridges.

picked as the near point of sampling and the standpipe was used as the site for the far sampling point. At each site, the 2-L samples were analyzed for free chlorine, dissolved oxygen, color, turbidity, pH, and temperature. Small aliquots from each sample were collected and preserved for total and filterable iron concentrations, ferrous iron concentrations, calcium and magnesium concentrations, total and filterable manganese concentrations, and alkalinity. All filterable samples were filtered in the laboratory of the Municipality of York Engineering Dept. and then preserved.

On days 1,3, and 5 samples were analyzed for free chlorine, color, turbidity, pH, and temperature. Samples were then collected from the 2-L sample and preserved for total, filterable, and ultrafilterable iron and manganese. Filterable samples were first passed through a 0.45 μm filter, in which a sample was collected, and the remainder passed through a 0.1 μm filter before preserving the samples. On day 1 sample 12 was placed in a water bath at 59° C to simulate water heater conditions and sample 13 was sparged with carbon dioxide gas to lower the pH to 7.0. On day 3, 500 ml of each sample, except for sample 12, were drawn for the streaming current analysis. After all samples had been collected over the five day period, iron, manganese, silica, calcium, and magnesium concentrations were determined by atomic absorption spectrophotometry (Tables 9 and 10).

Results of Oak Ridges Field Study

Only one sample showed better than 90% filterability through a 0.1 μm filter on day 1 (figure 43) and that was the treated sample representing the distant point in the distribution system. For the pH controlled sample and the near point treated sample, the filterability of the iron was greater than 70% through day 1. All samples had no greater than 53% filterability after day 1. The two worst cases of filterability were the raw and heated samples. Both of these samples dropped to below 20% after day 0 and were both consistently low throughout the test period. The pH-controlled sample showed the highest

Table 9. Five-day results from Oak Ridges iron stabilization field test in the presence of calcium and magnesium.[a] [b]

	Day 0							Day 1							Day 3							Day 5						
Sample[c]	Filterable Iron (%)	Total Iron (ppm)	Turbidity (FTU)	pH[d]	Color[e]	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)
10	42	1.54	0.0	7.8	5	50	0.035	6	1.41	14	7.6	0	148	0.031	9	1.43	14	7.4	48	115	0.033	6	1.42	14	7.5	110	109	0.033
11	43	1.58	0.0	7.7	0	50	0.028	47	1.55	0.82	7.6	0	21	0.028	6	1.54	1.1	7.6	0	40	0.030	3	1.57	1.1	7.7	16	29	0.014
12	43	1.58	0.0	7.7	0	50	0.028	3	1.53	0.87	7.5	0	32	0.031	2	1.99	0.98	7.5	30	50	0.032	3	1.56	0.90	7.5	22	69	0.016
13	43	1.58	0.0	7.7	0	50	0.028	77	1.60	0.54	7.5	0	79	0.029	53	1.61	0.79	7.0	0	88	0.025	5	1.57	0.97	7.2	22	60	0.025
14	71	1.57	0.0	8.3	0	100	0.021	76	1.60	0.63	7.6	0	85	0.026	29	1.61	0.89	7.7	1	83	0.024	3	1.60	0.88	7.9	16	66	0.030
15	99	1.55	0.0	8.3	0	100	0.022	54	1.57	0.73	7.5	0	81	0.026	11	1.56	0.88	7.7	5	71	0.024	5	1.53	0.92	7.8	15	50	0.030
	Water Heater sample																											
14	24	0.59				89	0.036																					

Alkalinity averaged 247 ppm as CaCO3 to the methyl orange end point.

[a] Sample 10 is the raw sample which had24 ppm as SiO2 naturally occurring. All other samples were treated with approximately 16 ppm as SiO2.

[b] Hardness totaled approximately 231 ppm as CaCO3 in the raw sample. Magnesium contributed 46 ppm as CaCO3.

[c] Sample 10 had 87% ferrous iron. All others were at 22% or less.

[d] The pH of all sample 13 was adjusted to 7.0 on each sampling day.

[e] Color is apparent color units.

Table 10. Filterability through a 0.45 µm filter

	Day 1		Day 3		Day 5	
Sample	Iron (%)	Manganese (%	Iron (%)	Manganese (%)	Iron (%)	Manganese (%)
10	2	116	1	79	2	91
11	98	89	22	47	3	92
12	1	32	1	104	1	88
13	99	86	97	75	1	44
24	100	119	53	67	8	50
25	91	117	22	72	5	47

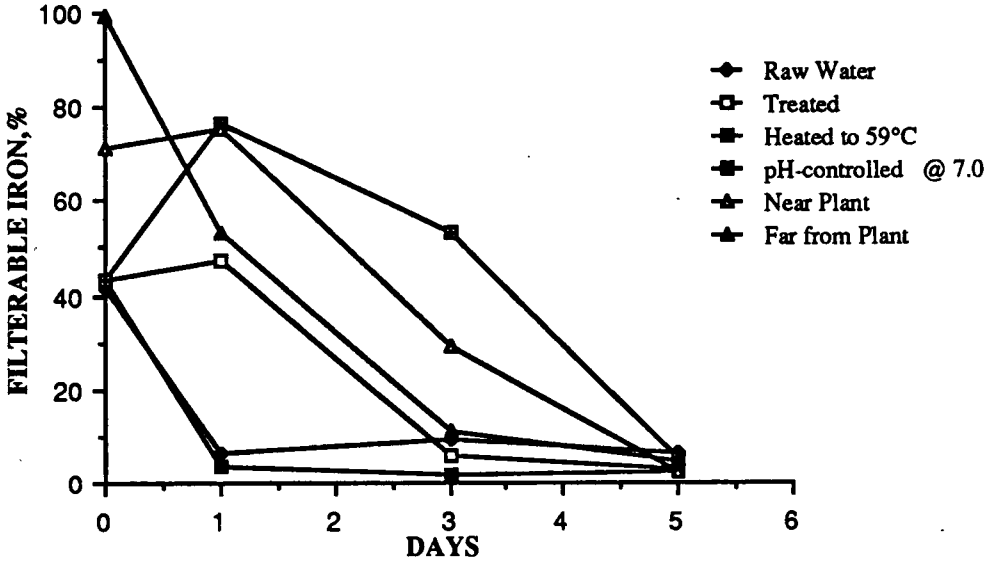


Figure 43. Filterable iron through a 0.1 μm filter from Oak Ridges, Ontario.

filterability after day 0. It should be noted that the treated samples from the distribution system had a higher iron filterability percentage than the treated samples from the pump station on day 0.

As the percentage of filterable iron decreased, color and turbidity increased and the total iron concentration fluctuated somewhat. The increase in color is very apparent with the raw and heated samples (figure 44). Turbidity is especially high for the raw sample which is recorded in the range of 14 NTU after day 0 (figure 45). Other samples only show a slight increase in turbidity for five days. On day 0 turbidity is measured with a HACH field kit which is calibrated in formazin turbidity units. The pH of the samples increase toward 8.0 (figure 46). The pH on day 0 is higher than on day 1 which may be due to faulty equipment. An electric current was running between the temperature electrode and the pH electrode producing erratic results. Therefore the pH was not temperature corrected. Total iron concentrations were relatively consistent for the treated samples but

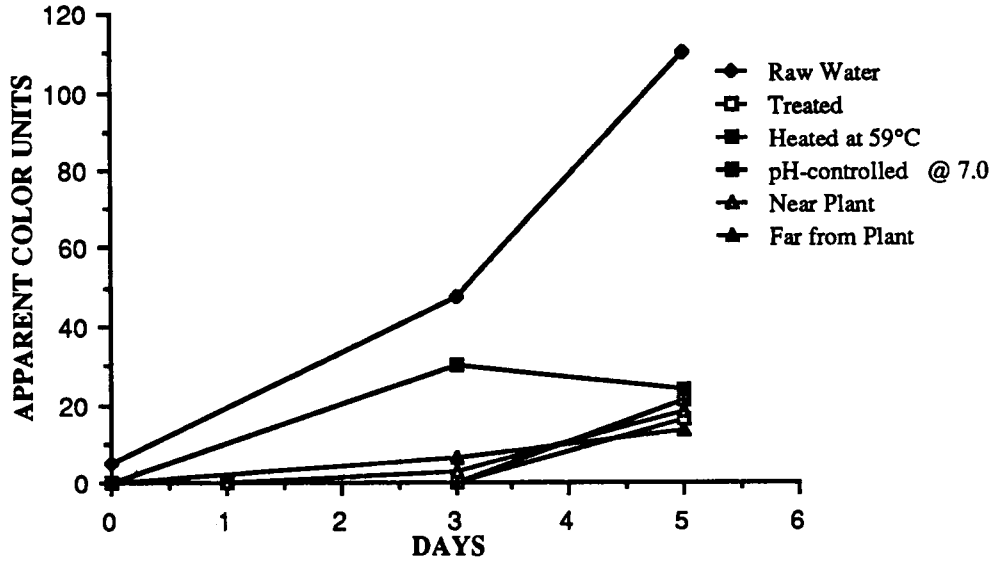


Figure 44. Apparent color of samples from Oak Ridges, Ontario.

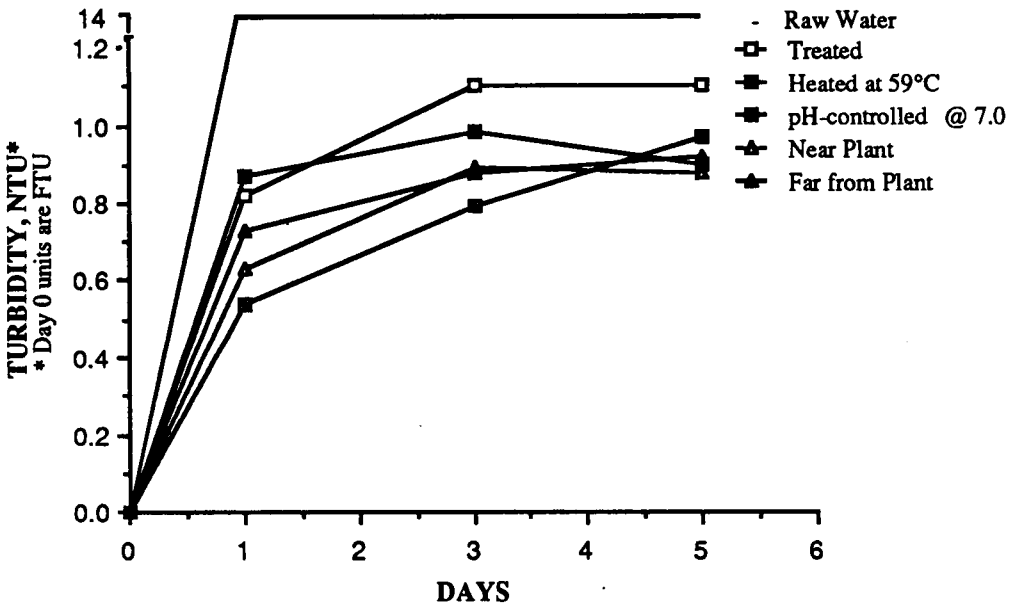


Figure 45. Turbidity of samples from Oak Ridges, Ontario.

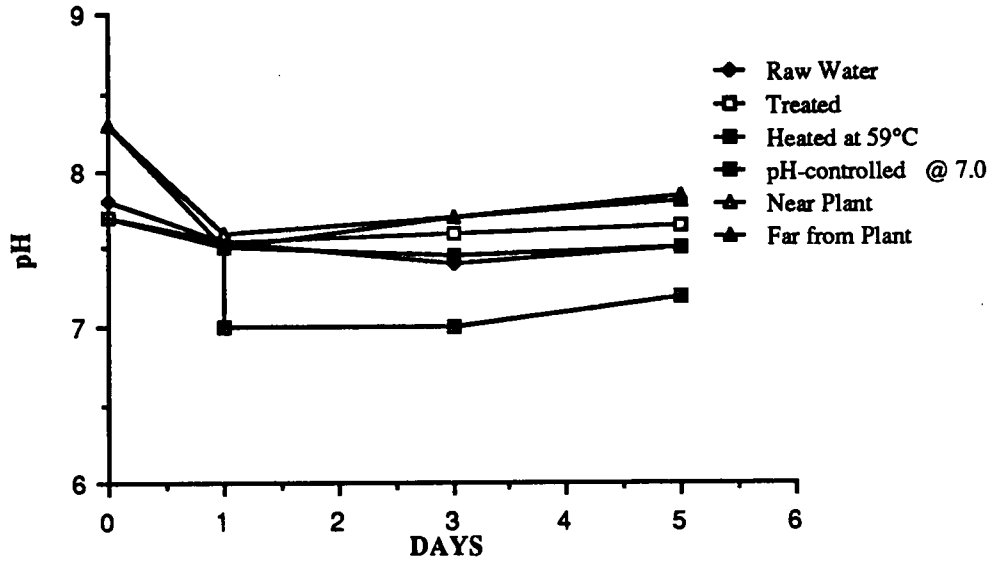


Figure 46. pH of samples from Oak Ridges, Ontario.

fluctuated for the heated sample and decreased for the raw sample (figure 47). The water heater sample collected from the Police Dept. had only one-third of the total iron of the raw and treated samples and showed only 24% filterability (Table 9). The iron filterability is very low when using a 1000 MW ultrafilter. The total iron concentration could not be accounted for by the mass balance of the filterant and the retainant. Therefore is is believed that part of the iron was trapped by the filter.

Filtered samples through a 0.45 μm filter contained over 90% of the total iron for the treated samples on day 1 but dropped to below 60% by day 3, except for the pH-controlled sample which stayed above 90% until day 5 (figure 48). Filterability for the raw and heated samples were below 10%. As with the 0.1 μm filter, the pH-controlled sample had the highest iron filterability percentage. Following the visual test conducted by M. O. E. for discoloration of the filters, no discoloration of the filters was present up to

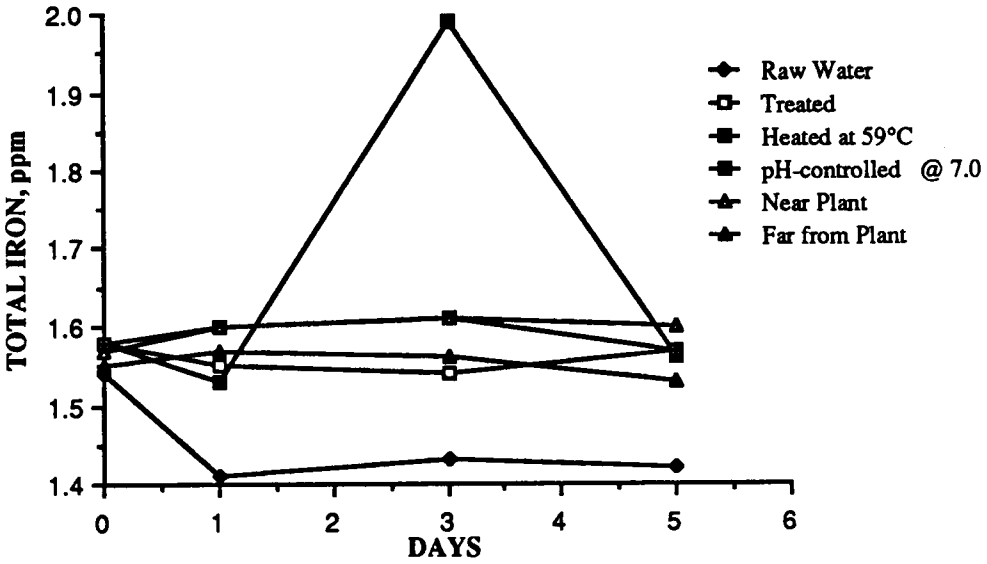


Figure 47. Total iron concentration of samples from Oak Ridges, Ontario.

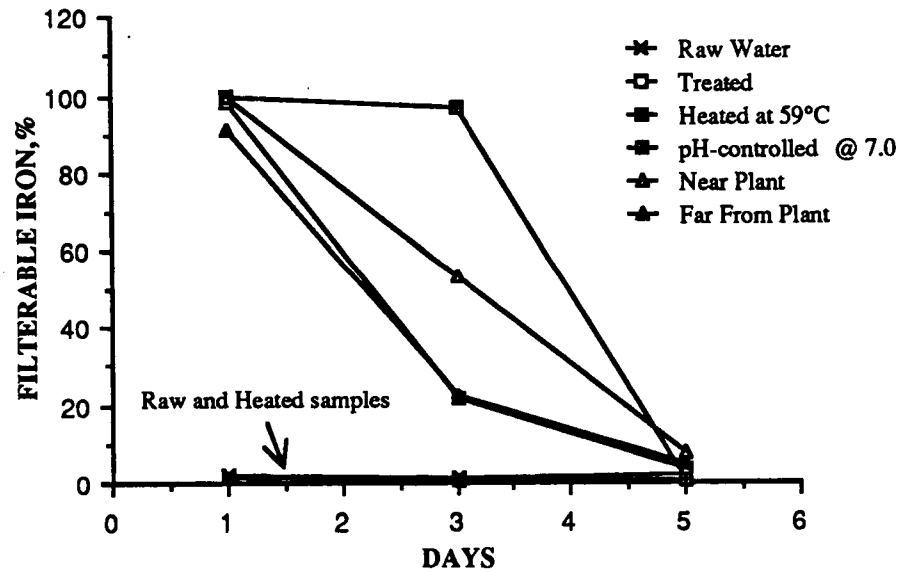


Figure 48. Filterable iron through a 0.45 μm filter at Oak Ridges, Ontario.

day 3 for all samples except for the pH-controlled sample which had a filter for day 5. The M. O. E. determines the breakpoint silicate dose when the white filters turn a yellowish-brown color, i. e. the lowest silicate dosage that leaves a clean white filter paper is chosen. Note that as expected, filterability was higher for the 0.45 μm filter membrane filter than for the 0.1 μm filter.

Manganese filterability results through a 0.1 μm filter and 0.45 μm filter were very erratic with some points greater than 100%. This could be due low concentration of manganese being close to the detection limits. At 1/1000 ppm a slight deviation in the concentration can produce high percentage differences between the total concentration and the filtered concentration. Even though the results were poor, they indicate that the raw sample has the highest filterability as compared to all of the treated samples (figures 49 & 50). Also the raw sample has a relatively more consistent total manganese concentration (figure 51).

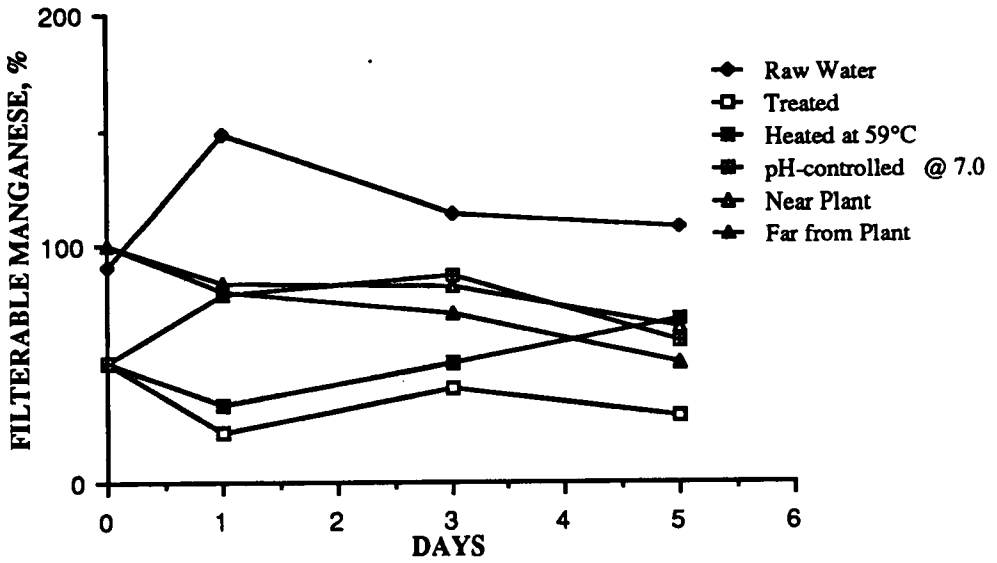


Figure 49. Filterable manganese through a 0.1 μm filter from Oak Ridges.

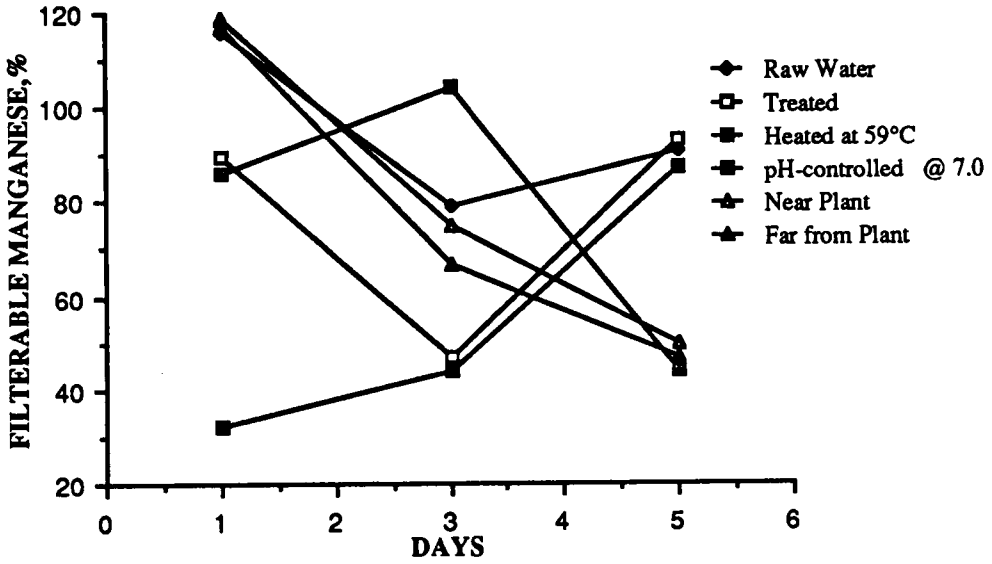


Figure 50. Filterable manganese through a 0.45 μm filter from Oak Ridges.

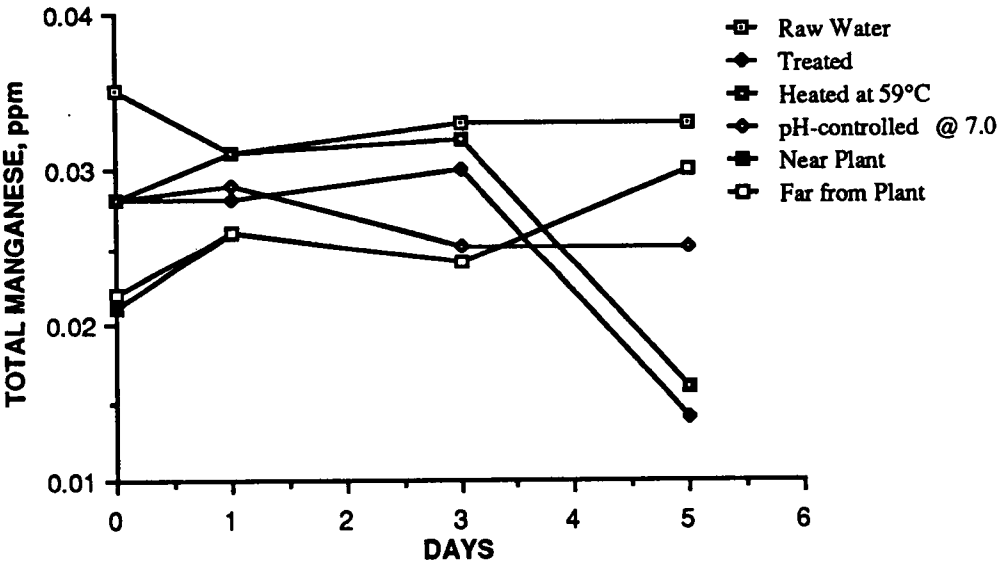


Figure 51. Total manganese concentration of samples from Oak Ridges.

Case History of Aurora [46]

The Aurora distribution system is approximately four times larger than the Oak Ridges system and serves a population of 28,000. The system consists of four wells and a total storage capacity of 5.22 MG (US) which is divided between two towers, one tank, and one reservoir. The geologic section in which the wells have been drilled is similar to that of Oak Ridges. The diagram of well number 2 (see Appendix) shows a mixture of clay, sand, and gravel with the well screen terminating in a gravel, sandy aquifer. An updated water quality analysis is presented in figure 54.

Prior to 1970, the town of Aurora did not treat their water. Late in 1970 both liquid chlorine (as hypochlorite) and sodium silicate were used as treatment due to complaints stemming from red water and odor. Complaints were minimized after the sodium silicate went on-line and the only red water complaints are from dead end mains and areas of low residual chlorine in outlying points along the distribution system. The hypochlorite was later converted to chlorine gas. Currently chlorine is injected at 2.5 - 3.0 mg/l prior to the addition of sodium silicate at a dosage of 8-10 mg/l at each well head. Additional chlorine is added at the southern and northern ends of the distribution system to maintain a chlorine residual at outlying points. York Engineering believes that chlorine residuals must be maintained to keep the iron sequestered. The sodium silicate is stored at approximately 70° F in a large underground storage tank.

Sampling Procedure at Aurora

As with the Oak Ridges, sampling took place at four predetermined sites. The raw sample and the three treated samples were drawn from taps at well number 2 which was on-line that day and pumping at 951 (US) gpm. Figure 53 lists the total monthly flows and the average pumping rate for each well for the past year. Also included are the total consumption of chlorine and sodium silicate. A water hose was not available for use

	Well #2	Well #3	Well #4
Iron, mg/l as Fe	0.760	1.30	0.770
Manganese, mg/l as Mn	0.038	0.048	0.040
Conductivity @ 25° C UMHO/CM	389.0	417.0	390.0
Total Hardness, mg/l as $CaCO_3$	193.0	216.0	184.0
Total Alkalinity, mg/l as $CaCO_3$	221.0	242.6	219.8
pH	8.51	8.42	8.45
Fluoride, mg/l as F	0.14	0.12	0.14
Chloride, mg/l as Cl^-	2.00	1.00	2.00
Sulfate, mg/l as SO_4	2.80	2.50	2.50
Nitrates, mg/l as N	0.10	0.10	0.15

Figure 52. Raw water analysis of Aurora by M.O.E. as of October 5, 1987.

1987 Monthly Flow	(US gal)	Chlorine Gas (lb)	N-Sodium Silicate (Imp. gal)
January -	101,719,460	2,887	2,570
February -	94,554,500	2,686	2,322
March -	109,004,810	2,906	2,981
April -	111,393,480	2,739	2,699
May -	132,503,970	2,655	2,797
June -	132,797,560	2,331	3,142
July -	132,582,120	2,515	2,580
August -	138,743,350	3,093	2,828
September -	122,860,580	2,451	2,477
October -	115,593,980	2,269	2,140
November -	112,400,640	1,589	2,294
December -	106,790,640	2,280	2,130
Totals -	**1,410,945,100**	**30,399**	**31,876**

Average Yearly Flow = 3,780,000 US gpd

No. 1 Well Flow = 600 gpm

No. 2 Well Flow = 960 gpm

No. 3 Well Flow = 1100 gpm

No. 4 Well Flow = 1500 gpm

Figure 53. Total monthly flows and average flows for each well in Aurora for 1987.

during the sampling at this location.The near sampling point was a booster station and the far sampling point was the storage tank, where a water hose was employed to reduce aeration. A water heater sample was taken at the well station. Day 0 procedures at Oak Ridges were followed also at Aurora.

On days 1, 3, and 5 the same procedure as with the Oak Ridges samples were followed. Sample 18 was placed in the water bath and sample 19 was reduced to pH 7.0 on day 1. Streaming current samples were taken on day 3 from all samples except the heated sample 18 (tables 11 and 12).

Results of Aurora Field Study

Aurora iron filterability was superior to Oak Ridges filterability, where iron filterability was greater than 90% for three days through a 0.1 μm filter under normal conditions and for five days at pH 7.0 (figure 54). For the sample representing a far point in the system, the filterability percentage dropped below 90% after day 1. Poorest filterability resulted with the raw sample and the heated sample. Both of these had filterabilities below 20%. After day 3 all treated samples significantly dropped in filterability.

Low turbidity and low color values (figures 55 and 56, respectively) are apparent for the treated samples, and the samples have a constant total iron concentration (figure 57). Turbidities for the treated samples ranged between 0 - 0.56 turbidity units whereas the raw sample was above 1 NTU for the five day period. The heated sample consistently had a slightly higher turbidity than the other treated samples. The apparent color of the raw water was low but the treated samples were relatively much lower by comparison. As with turbidity, the color of the heated sample became slightly higher by day 5 than the rest of the treated samples. Total iron for all treated samples except for the heated sample were relatively constant. The heated sample had a fluctuating total iron concentration while the

Table 11. Five-day results from Aurora iron stabilization field test in the presence of calcium and magnesium.[a] [b]

Sample [c]	Day 0							Day 1							Day 3							Day 5						
	Filterable Iron (%)	Total Iron (ppm)	Turbidity (FTU)	pH [d]	Color [e]	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterable (%)	Manganese Total (ppm)	Filterable Iron (%)	Total Iron (ppm)	Turbidity (NTU)	pH	Color	Manganese Filterability (%)	Manganese Total (ppm)
16	29	0.77	0.0	7.9	0	76	0.038	6	0.73	2.6	7.8	0	103	0.033	9	0.65	2.3	7.9	0	92	0.036	11	0.62	2.2	8.1	23	113	0.032
17	100	0.85	0.0	8.0	0	100	0.039	98	0.86	0.24	7.7	0	107	0.042	95	0.87	0.30	7.8	0	97	0.038	34	0.89	0.56	7.9	2	56	0.027
18	100	0.85	0.0	8.0	0	100	0.039	3	0.87	0.48	7.6	0	25	0.042	2	1.06	0.54	7.7	0	26	0.043	3	0.87	0.64	7.9	13	24	0.038
19	100	0.85	0.0	8.0	0	100	0.039	97	0.88	0.23	7.7	0	76	0.049	95	0.87	0.27	7.1	0	97	0.037	88	0.88	0.34	6.6	4	83	0.041
20	100	0.82	0.0	7.9	0	89	0.038	97	0.85	0.34	7.8	0	102	0.042	94	0.84	0.37	7.9	0	105	0.038	42	0.85	0.45	8.0	6	64	0.039
21	99	0.75	0.0	7.9	0	92	0.038	92	0.77	0.28	7.8	0	110	0.039	85	0.79	0.37	7.9	0	93	0.030	47	0.77	0.51	8.0	3	77	0.031
	Water Heater sample																											
17	50	0.04				33	0.018																					

Alkalinity averaged 200 ppm as CaCO3 to the methyl orange end point.

[a] Sample 16 is the raw sample which had 22 ppm as SiO2 naturally occurring. All other samples were treated with approximately 11 ppm as SiO2.

[b] Hardness totaled approximately 175 ppm as CaCO3 in the raw sample. Magnesium contributed 46 ppm as CaCO3.

[c] All samples had 40% ferrous iron or less.

[d] The pH of all sample 19 was adjusted to 7.0 on each sampling day.

[e] Color is apparent color units.

Table 12. Filterability through a 0.45 µm filter

Sample	Day 1		Day 3		Day 5	
	Iron (%)	Manganese (%	Iron (%)	Manganese (%	Iron (%)	Manganese (%)
16	0	91	0	72	8	88
17	100	91	97	74	84	119
18	0	7	2	33	2	24
19	99	82	97	73	95	71
20	99	83	96	100	94	105
21	99	95	91	90	94	84

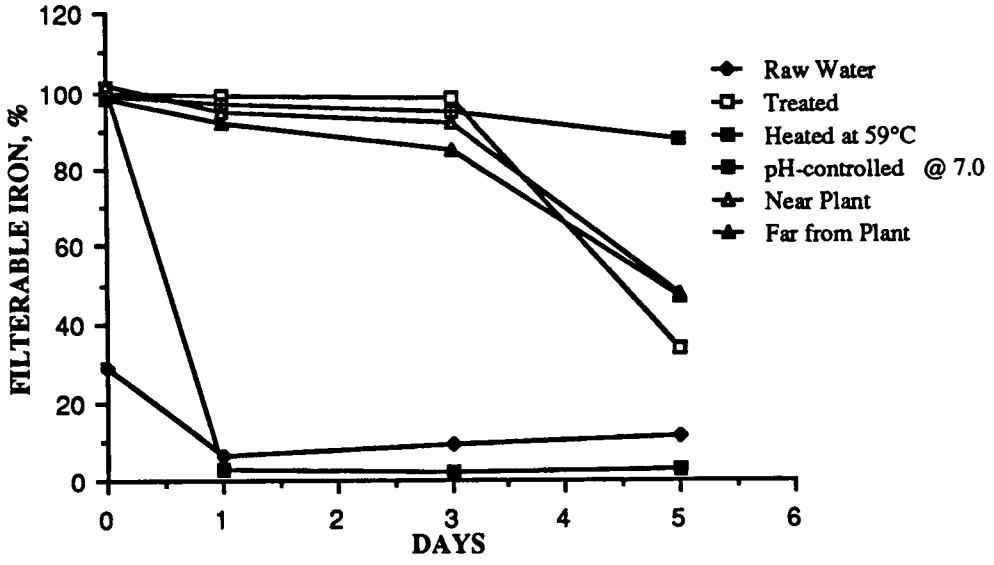


Figure 54. Filterable iron through a 0.1μm filter from Aurora, Ontario.

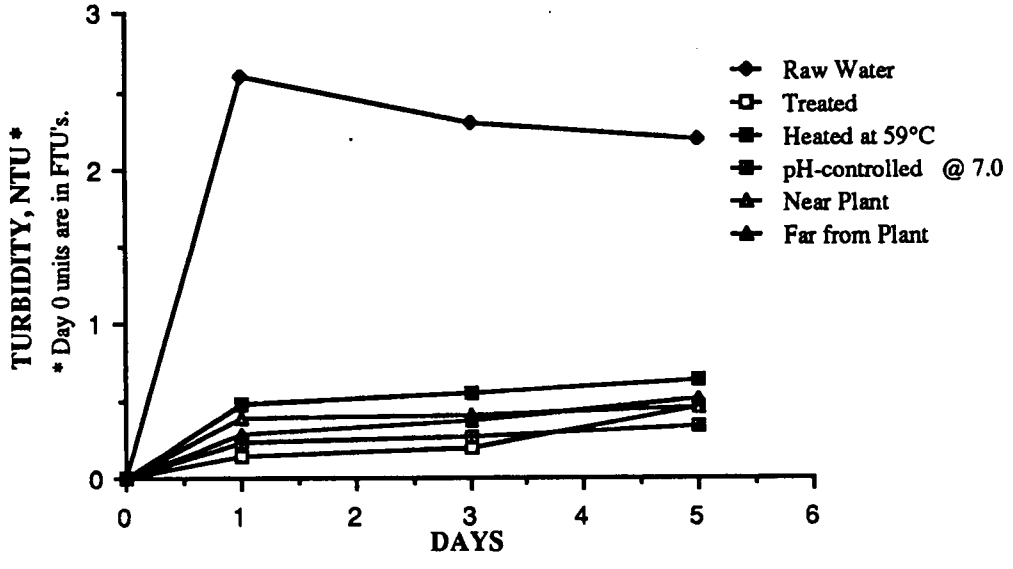


Figure 55. Turbidity of samples from Aurora, Ontario.

raw sample decreased in total iron. The sample taken from the hot water tap had only 5% of the total iron of the raw water and exhibited 50% filterability through a 0.1 μm filter. The pH of all samples rose toward pH 8.0 except for the pH-controlled sample (figure 58). Similar problems with the ultrafiltration test from Oak Ridges occurred with the Aurora test. The mass balance of the filterant and retainant could not account for all of the iron. Iron was probably trapped on the filter but still some iron did pass through the 1000 MW filter.

The filterability test using a 0.45 μm filter (figure 59) shows better than 90% iron filterability for five days with all of the successfully treated samples except for the unaltered treated sample, which dropped below 90% after day 3. Discoloration of the filters were only slight and would pass the visual filter test of the Ontario Ministry of Environment. As for the raw and heated samples, filterability was below 10% and lower than the filterable percentages through the 0.1 μm filter but within experimental error.

As with the Oak Ridges test, manganese results also had filterabilities greater than 100% for some of the data points. All samples had greater than 75% filterability up to day 3 through the 0.1 μm filter (figure 60) and for five days through the 0.45 μm filter (figure 61) except for the heated sample which dropped to below 35% after day 1. All samples were relatively consistent for the total manganese concentration (figure 62).

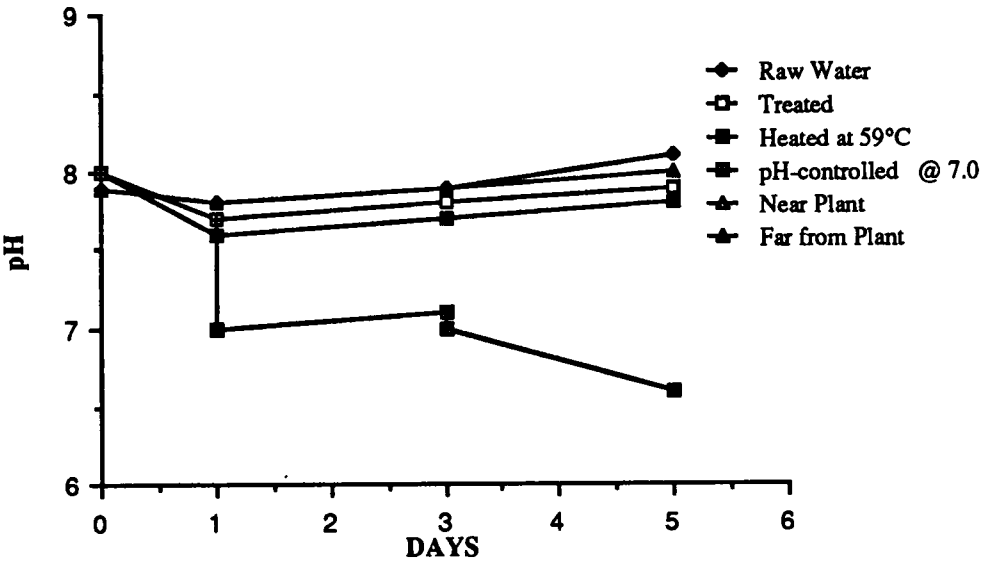


Figure 58. pH of samples from Aurora, Ontario.

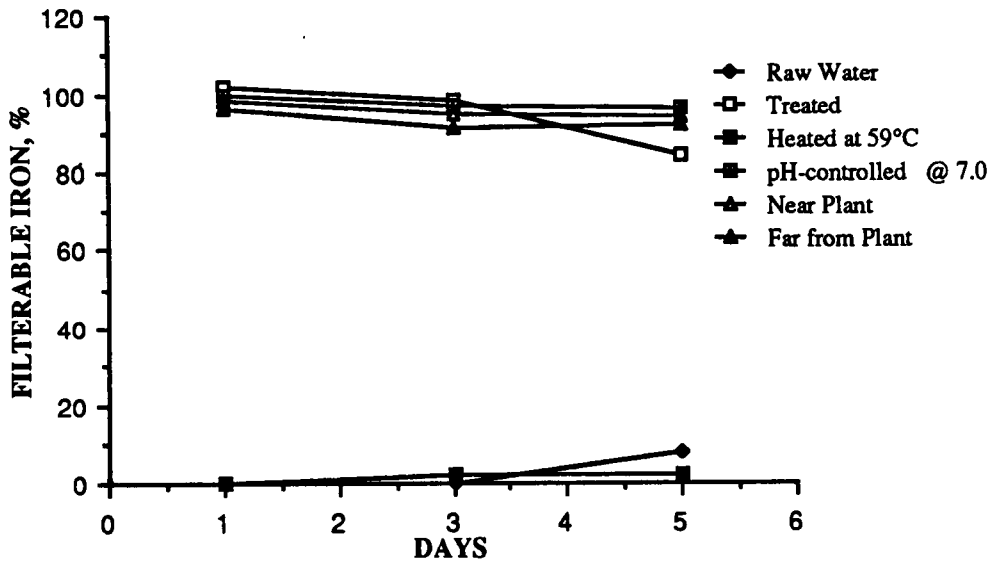


Figure 59. Filterable iron through a 0.45 μm filter from Aurora, Ontario.

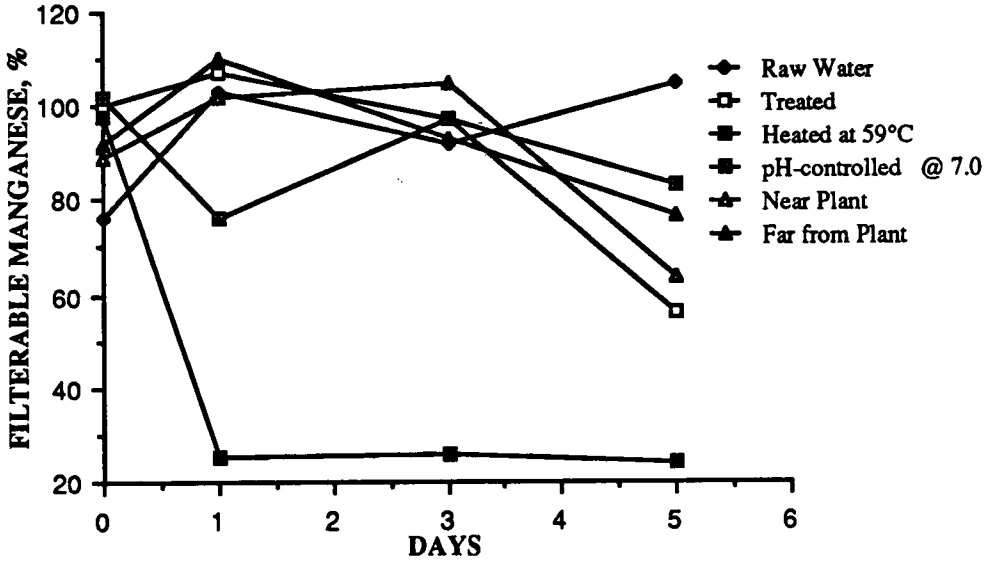


Figure 60. Filterable manganese through a 0.1 μm filter from Aurora.

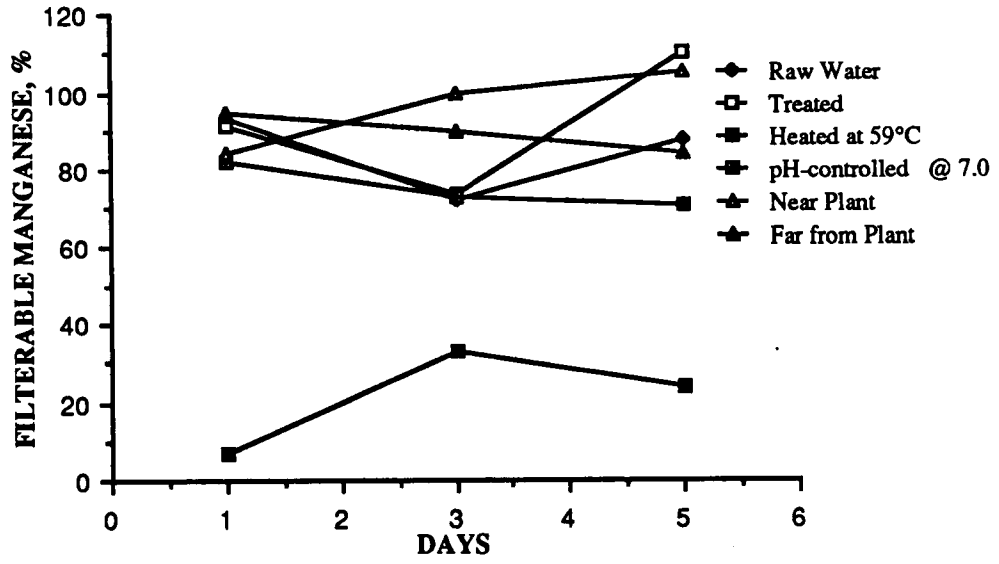


Figure 61. Filterable manganese through a 0.45 μm filter from Aurora.

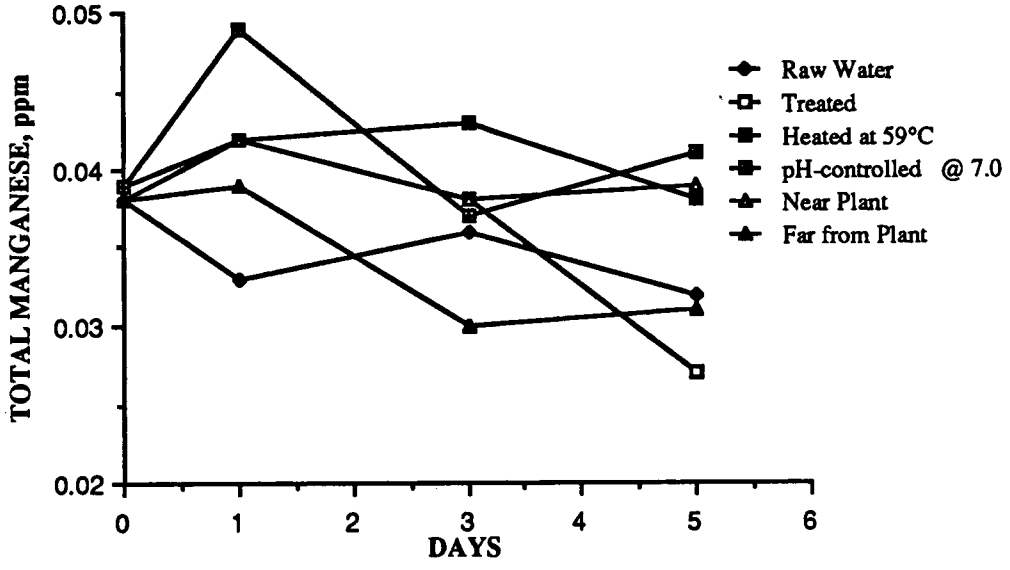


Figure 62. Total manganese concentration of samples from Aurora, Ontario.

V. DISCUSSION OF RESULTS

Whether in the presence or absence of calcium, iron filterability decreases over time. Previous works [6,35] and the field studies [Figures 32, 36, 44, and 56] both show a decline in iron filterability with time proving that sequestration is only a temporal effect. The poor treatment at the far ends of Oak Ridges's system, even though filterability was high through the 0.45 μm filter on day 0 and 1, may be the result of long detention times.

Laboratory tests show that calcium definitely has an adverse effect on iron stabilization. For example, at sodium silicate dosages of approximately 12 ppm as SiO_2 and at 8 ppm $CaCO_3$ or less, stabilization occurred for three days, i. e. ≥ 90% filterability (Figure 5),and low turbidity, but at concentrations of 175 ppm $CaCO_3$ and greater, which are common hardness values for groundwater, iron stabilization was suppressed to less than one day. The effect of calcium could be the possible cause of consumer complaints in distribution systems with a one day residence time or longer.

The field studies of the villages of Waukesha and Butler public water supplies exhibited the adverse effect of high hardness values on the sodium silicate sequestration of iron. The Wisconsin iron filterabilities (Figures 32 and 36) indicate that 12-15 ppm as SiO_2 can only stabilize the iron up to day 1 or less in the presence of 175 ppm or more of hardness as $CaCO_3$. In the absence of calcium, this dosage level stabilized iron up to day 5 in Browman's work [6]. Under similar conditions to the Wisconsin studies, 32 ppm as SiO_2, which includes the background silica of the raw water, at Aurora (Figure 54) increased stabilization to day 3. Laboratory tests (Figure 5) and Robinson, et. al. [35] indicate that hardness values ≥ 50 ppm as $CaCO_3$ decrease the period of iron stability to one day . Therefore higher sodium silicate dosages are a possible solution to increase the effectiveness of treatment (Figure 11).

When compared to test 1, test 2 shows that by doubling the SiO_2 dosage from 12 ppm to 24 ppm, successful treatment can be lengthened from 3 to 5 days when $CaCO_3 \leq$ 45 ppm. Even with doubling of the SiO_2 dosage, treatment will not last for one day when $CaCO_3 \geq 93$ ppm. Therefore, unacceptably high silica dosages would be necessary to extend treatment beyond one day at these higher calcium levels. For example, test 4 had five days of iron filterability $\geq 90\%$ at 155 ppm as $CaCO_3$ and a dosage of 38 ppm as SiO_2 (Figure 17) but Oak Ridges only had one day of high iron filterability at 250 ppm as $CaCO_3$ and at a similar silica concentration, which included the dosage plus the silica background. These comparisons indicate that a water utility could increase the SiO_2 feed rate to counteract the inhibitive effects of lower concentrations of calcium ions on treatment but that high calcium concentrations remain a serious limitation of treatment in laboratory experiments.

From the results of test 4 and the field studies, one can conclude that higher silicate dosages and neutral pH values as compared to higher pH are beneficial to sodium silicate sequestration in the presence of high concentrations of calcium. By tripling the silicate dosage from $\approx$ 13 ppm (test 11) to $\approx$ 33-38 ppm as SiO_2 and controlling the pH at 7.0, the stabilization period can be increased to five days in the presence of 155-157 ppm as $CaCO_3$ when compared to samples at pH 8.0 (Figure 17). Even though stabilization failed at lower dosages, turbidities $\leq$ 1 NTU occurred (Figure 18), which were below the 1 NTU EPA standard and also the limit of 2 NTU acceptable by Camp Dresser and McKee, Inc.

For all field systems (Figures 36, 44, and 56), except for Waukesha (Figure 32), the best iron filterability occurred after a treated sample was maintained at pH 7.0. These results contradict the laboratory works of Browman [6] and Dart and Foley [9,10], who found that better treatment occurred at pH 8.0.

Browman's better results at higher pH were under differing conditions which involved the dilution of the silicate dosage and without the presence of calcium ions. Since

it is believed that calcium effects stabilization according to the Schulze-Hardy rule [35], it is not clear how pH could effect the destabilization power of calcium because only a small fraction is complexed at either pH 7 or 8 [35] and the particle charge ought not to change significantly over this pH range either.

Robinson, et. al. [35] performed a complete speciation of example waters without iron using the MINTEQ geochemical equilibrium model program. They noted that only a slight complexation occurred between calcium and silicic acid at pH 7 and pH 8, but at pH 8 the reaction was 100-fold stronger. This author hypothesizes that possibly silica polymers could interact with calcium, similarly to silicic acid, but forming calcium-silica complexes of higher concentrations which could account for poor treatment at pH 8.0. Detailed experiments would be required to support or refute this hypothesis.

Laboratory work by Browman [6] found that long lag times during treatment produce poor results. The drop in iron filterability after day 0 at Ranielle (Figure 22) supports Browman's data and the conclusion of Dart and Foley [9] which indicate that long lag times between the injections of sodium silicate and chlorine are not conducive to iron stabilization.

Low filtered iron and manganese for all heated samples (Figures 32, 36, 44, and 56) indicate that high temperatures, which are common to a water heater, breakdown the sequestering effect. The unheated samples had much higher iron filterabilities. A visible precipitate was noticed in each of the heated samples indicating flocculation of the iron and manganese. This thermal breakdown in treatment would explain the occasional red water complaints during the use of hot water taps.

A new parameter measured in this field test is the filtration of iron and manganese through a 0.45 μm filter. According to this test, sequestration occurred for three days for Oak Ridges (Figure 48) and for five days at Aurora (Figure 59). From this data, over 80% of the iron and manganese precipitates are less than 0.45 μm in size for up to three days,

which is well below the visible detection limit of 8 μm [45]. This higher filterability can be contrasted with the lower iron filterability through the 0.1 μm filter which was less than 60% on day 3 at Oak Ridges as well as on day 5 at Aurora. This suggests that low filtered iron concentrations through a 0.1 μm filter may not necessarily indicate failed sequestration depending on the iron concentrations and residence times. Evidence of this can be found at Waukesha which had low iron levels and where filterability is around 40% through a 0.1 μm filter (Figure 32) but complaints are still at a minimum. However, if low filterabilities are seen through a 0.1 μm filter, then low filterabilities will surely be found through a 0.45 μm filter in time.Since there are no major complaints by customers of iron containing particulates ranging in size of 0.1-0.45 μm, future field tests should be compatible to water utility tests and include filtration through a 0.45 μm. This will enable better comparisons with the results of the utility's field data and include a parameter which could be an upper limit of acceptable treatment in laboratory studies for waters of low iron concentrations.

The Oak Ridges raw water had the highest manganese filterability (Figure 49) than did the treated samples. The oxidation of manganese by chlorine is too slow for the oxidized manganese to react with silica before depolymerization. Therefore the oxidized manganese precipitates out of solution. The high filterability of the untreated Oak Ridges sample supports Robinson and Ronk's findings [38] that no treatment is better for manganese stabilization than actual treatment.

VI. CONCLUSION

Field studies indicate that laboratory results are correlating with results in the field. The sites documented for this study appear to be meeting general consumer satisfaction with only a few problems at the far ends of the distribution system and in water heaters. From these results the following conclusions have been made.

1. Both field and laboratory results indicate that stabilization is only temporal. This could explain the problems found at the ends of some of the systems studied.

2. Both field and laboratory results show that calcium reduces the length of the already temporary stabilization.

3. Laboratory tests indicate that an increase in the silica dosage increases the length of treatment in the presence of calcium.

4. The field and laboratory results show that long lag times between the silicate and chlorine dosages are not efficient to treatment.

5. Stabilization breaks down faster at elevated temperatures. Iron precipitates out of water heaters causing some complaints. The practise of flushing of the water heaters temporarily solves this problem. Laboratory studies showed that on the average heated samples had higher turbidities and color and lower filterable iron than treated samples at normal temperatures.

6. The 0.45 μm filter results correlated slightly better with actual field practices than the 0.1 μm filter results. Even with low filterability through the 0.1 μm filter, few complaints were recorded by the utilities. In some cases when low filterability occurred with the 0.1 μm filter, filterabilities > 90% were still obtainable through the 0.45 μm filter. Therefore low filterability through a 0.1 μm filter does not necessarily indicate failed sequestration. Suggest the use of the 0.45 μm filter over the 0.1 μm filter in future field tests.

7. Manganese field studies indicate that no treatment, albeit unfeasible, is better than the sodium silicate-chlorine treatment which is consistent with laboratory studies. However, chlorination for disinfection is mandatory for most utilities which may cause manganese related problems.

8. Previous results of laboratory studies have been shown to closely model field conditions.

9. Laboratory results with high pH are conflicting with previous studies. High pH showed worse treatment whereas previous work showed best treatment at high pH. Possibly the presence of calcium, predilution of silicates, or different ages of silicate solutions are some of the possible reasons for this conflict.

10. Objective scientific field studies are able to characterize and quantify the success of sequestration at field sites.

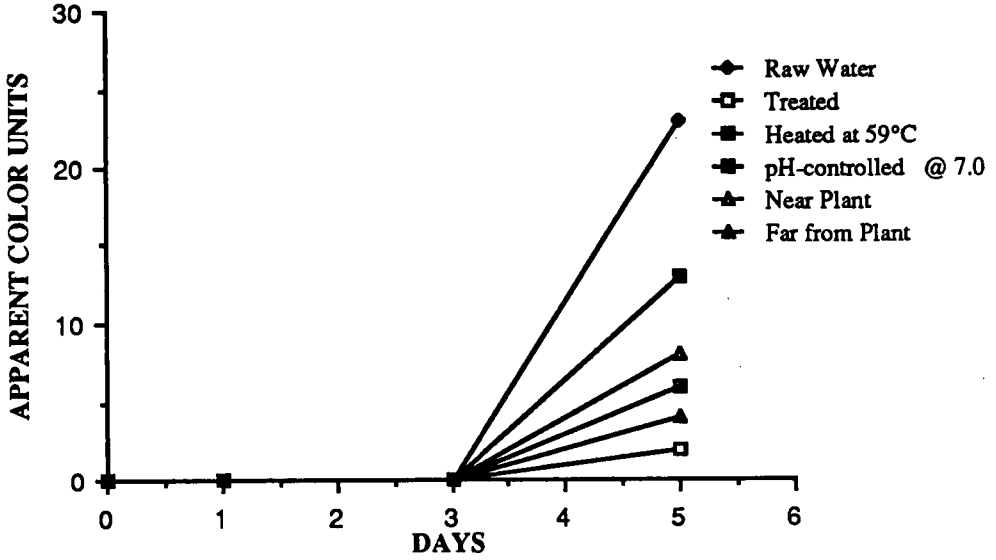


Figure 56. Apparent color of samples from Aurora, Ontario.

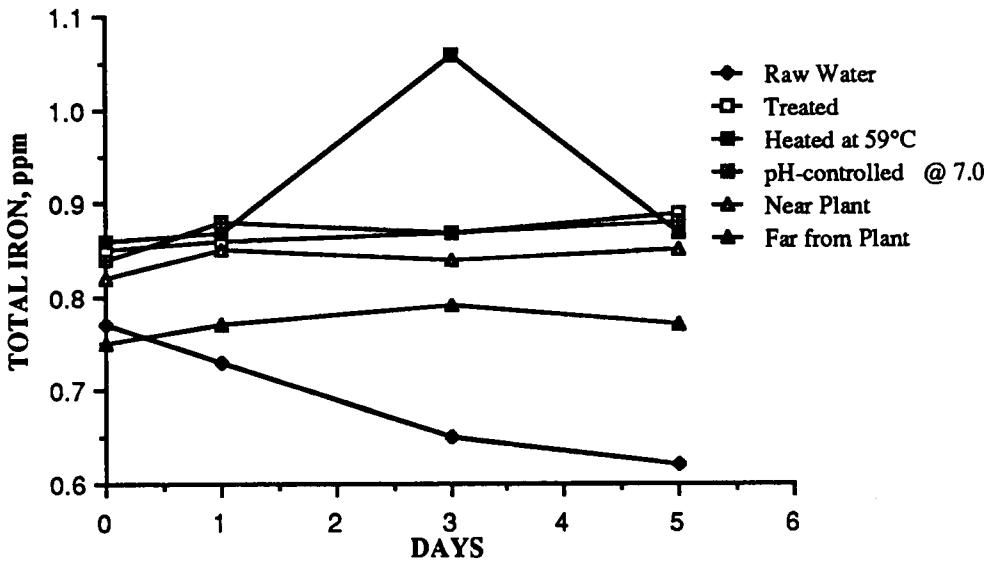


Figure 57. Total iron concentration of samples from Aurora, Ontario.

VII. RECOMMENDATIONS FOR FURTHER STUDIES

The following recommendations are suggested for further work in iron and manganese sequestration.

1. A more viable manganese treatment is needed rather than practising no treatment. Possibly the use of a stronger oxidant will provide an avenue to better treatment.

2. The interaction of sodium silicate, iron, and manganese on the level of surface charge interaction should be closely studied.

3. A cost analysis between sodium silicate and polyphosphates is needed to determine which of the two sequesterants are more economical.

4. A study of potassium silicate as a feasible substitute for sodium silicate in areas of high sodium concentrations in the drinking water. Sodium silicate dosages can increase the sodium concentration above the suggested limits for consumers with high blood pressure.

5. In future field studies the use of the 0.45 μm filter over the 0.1 μm filter is suggested for more compatible results with actual field practises.

6. The possibility of iron oxidation within the pump should be considered. Through personal communication, a local well driller noted that oxidation of iron had occurred within the casing of some wells which had been pulled for servicing.

7. A study of the effects of sequestration on public and private pools, laundry mats, and other locations in which chlorine is used at high concentrations.

BIBLIOGRAPHY

1. Sawyer, C.N. and P.L. McCarty. *Chemistry for Sanitary Engineers* . Second ed. McGraw-Hill Book Company, New York. 518 pp. 1967.

2. Viessmann, W., Jr. and M.J. Hammer. *Water Supply and Pollution Control* . Fourth ed. Harper and Row, Publishers. New York. 797 pp. 1985.

3. U. S. Environmental Protection Agency. National Secondary Drinking Water Regulations. *Fed. Regis.* 42: 17144-17147. 1977.

4. Holden, J.M. Treatment of Iron Bearing Groundwaters by the simultaneous Addition of Sodium Silicate and Sodium Hypochlorite. M.S. thesis, unpublished. The University of Tennessee, Knoxville, TN. 197 pp. 1985.

5. Stiles, J.F., III. Survey of the Iron and Manganese Problems in the USA. Proceeding of the Annual Conference AWWA. 1978.

6. Browman, M.G. Role of Silica Polymerization in the Treatment of Iron Bearing Groundwater by the addition of Sodium Silicate and Sodium Hypochlorite. M.S. thesis, unpublished. The University of Tennessee, Knoxville, TN. 193 pp. 1986.

7. Klueh, K.G. and R. B. Robinson. Sequestration of Iron in Groundwater by Polyphosphates, in press J. Environmental Engineering Division, ASCE.

8. Robinson. Sequestering Methods of Iron and Manganese Treatment. Quarterly progress report.for AWWARF. June 1987.

9. Dart, F.J. and P.D. Foley. Preventing Iron Deposits with Sodium Silicate. J. AWWA 62 (10): 663-668. 1970.

10. Dart, F. J. and P.D. Foley, Silicate as Fe, Mn Deposition Preventative in Distribution Systems, AWWA, 64 (4): 244 - 249, 1972.

11. Stumm, W. and J.J. Morgan. *Aquatic Chemistry*. Second ed. John Wiley & Sons Inc. New York, NY. 1981.

12. Camp Dresser and McKee Inc. Memo to R.B. Robinson. Feb. 1987.

13. Committee Report: Research Needs for the Treatment of Iron and Manganese. J. AWWA 79 (9): 119-122. 1987.

14. Weber, W.J., Jr. *Physicochemical Processes for Water Quality Control.* John Wiley & Sons, Inc. 640 pp. 1972.

15. Robinson, The Iron Precipitate in Groundwater Supplies. . 1979.

16. Schwertman, U. and R.M. Taylor. The Transformation of Lepidocrocite to Goethite. Clays Clay Min. 20: 151-158. 1972.

17. Snoeyink, V.L. and D. Jenkins. *Water Chemistry* . John Wiley & Sons Inc. New York. 463 pp. 1980.

18. Hurlbut, C.S., Jr. and C. Klein. *Manual of Mineralogy.* Nineteenth ed. John Wiley & Sons, New York. 532 pp. 1977.

19. Iler, R.K. *The Chemistry of Silica* . John Wiley & Sons, New York. 866 pp. 1979.

20. O'Conner, T.L. The Reaction Ratio of polysilicic acids with Molybdic Acid. J. Phys. Chem. 65: 1-5. 1961.

21. McGarry, M.R., and J.F. Hazel. Electron Microscopy of Labile Alkali Silicate Solutions. J. Colloid Sci. 20: 72-80. 1962.

22. Hazel, J.F. Lability of Aqueous Solutions of Potassium Silicate. J. Colloid Sci. 19: 162-168. 1962.

23. Lehrman, L., and H.L. Schuldner. The Role of Sodium Silicate in Inhibiting Corrosion by Film Formation on Water Piping. J. AWWA 43 (3): 175-188. 1951.

24. Hazel, J.F., Schock, R.U., Jr., and Gordon, M. Interaction of Fe^{2+} ions with Silicic Acid. J. Am. Chem. Society. 71 (6): 2256-2257. 1949.

25. Weber, W.J. and W. Stumm. Formation of a Silicato-iron (III) Complex in Dilute Aqueous Solution. J. Inorg. Nuclear Chem. 27: 237-239. 1965.

26. Olsen, L.L., and C.R. O'Melia. The Interaction of Fe (III) with $Si(OH)_4$. J. Inorg. Nuclear Chem. 35: 1977-1985. 1973.

27. Schenk, J.E., and J. Weber. Chemical Interaction of Dissolved Silica with Iron (II) and (III). J. AWWA. 60 (2): 199-212. 1968.

28. Tamura, H., K. Goto, and M. Nagayama. Effects of Anions on the Oxygenation of Ferrous Iron in Neutral Solutions. J. Inorg. Nuclear Chem. 38: 113. 1976.

29. Robinson, R.B., M.B. Browman, and G.D. Reed. On Chemical Principles of Iron Control by Sodium Silicate and Sodium Hypochlorite.

30. Hazel, J.F., W.M. McNabb, and P.E. Machemer. A Potentiometric Study of the Interaction of Zinc Ions with Sodium Silicates. J. Electrochemical Society. 99 (7): 886-896. 1950.

31. Falcone, J.S. The Effects of Degree of Polymerization of Silicate on their Interaction with Cations in solution. *Proceedings of the symposium on Soluble Silicates.* Am. Chem. Society. 194: 79-93. 1982.

32. Heaney, P.A., and W.F. Hyslop. Manganese Sequestration - The Prince George Experience. A paper presented to the British Columbia Water and Waste Association. April 1986.

33. Henry, C.R. Prevention of the Settlement of Iron. J. AWWA. 42 (9): 886-896. 1950.

34. Dart, F.J. Recent Developments in Iron and Manganese Control. Annual Conference Seminar on the Control of Inorganic Contaminants, pp 1 - 20, 1983.

35. Mirando, L. and R.C. Marini. Improving Water Quality at the Long Island Water Corporation, New York.

36. Robinson, R.B., R.A. Minear, and J.M. Holden. Effect of Several Ions on Iron Treatment by Sodium Silicate and Hypochlorite. J. AWWA. 79 (7): 116-125. 1987.

37. Robinson, M.G. Browman, and Holden. Iron and Manganese Treatment by the Addition of Sodium silicate and Chlorine, unpublished.

38. Robinson and S. Ronk. The Treatability of Manganese by Sodium Silicate and Chlorine. J. AWWA. 79 (11): 64-70. 1987.

39. Lee, G. F. and W. Stumm. Determination of Fe^{2+} in the presence of Fe^{3+} with Bathophenanthroline. J. AWWA. 52 (12): 1567-1574. 1960.

40. APHA, AWWA, WPCF. *Standard Methods for the Analysis of Water and Wastewater*. Sixteenth ed. APHA, Washington, D.C. 1985.

41. Ranielle, W. Va. Water Dept. files. 1987.
42. JMM

43. Waukesha, Wis. Water Utility files. 1987.

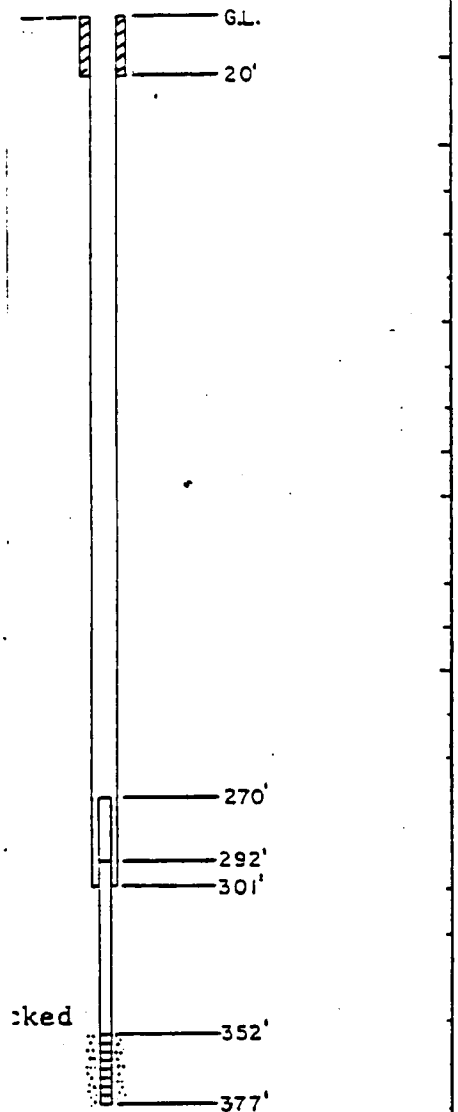
44. Barrett, B.S. Iron Sequestration with Sodium Silicate, unpublished. October 1974.

45. Bionomics Corp. Sodium Silicate Addition, unpublished. Submitted to Butler Water Utility. June 1976.

46. Sedore, D. Personal compilation of history of Aurora and Oak Ridges, Ontario Water Departments, unpublished. 1988.

APPENDIX

sketch of well



details of well

Well no. 1 Use Municipal
Municipality Oak Ridges County York
Driller M. Abbott Date June 27/61
Guaranteed or designed capacity 300 GPM
Well type gravel wall diameter 20-inch
depth from G.L. 377 ft. from B.P.
Elevation G.L. B.P.

WELL MATERIALS

Outer casing 301 feet of 20-inch diameter
Inner casing 107 feet of 10-inch diameter
Screen 10 inch diameter stainless shutter
Plug
Gravel silica Grout cement to 20 ft

WELL HYDRAULICS

Original static level 62.5 ft. Date July 3/61
Pumping rate 325 GPM Date
period 72 hours level 83 feet
Changes in discharge rate

Water level recovery period 24 hours
Aquifer type depth
Permeability 1,370 gpd/ft^2
Coefficient of transmissibility 41,000 gpd/ft.
Coefficient of storage 3.5×10^{-5}

WATER QUALITY

Hardness 260-70 Alkalinity 266-76 Iron 1.6-1.8
Chloride 1-8 pH 7.7-7.9
Sulphates Trace

RECOMMENDED SETTINGS

Pumping rate
Pump setting G.L.-M.B.
Other -

ONTARIO WATER RESOURCES COMMISSION

TOWNSHIP OF KING

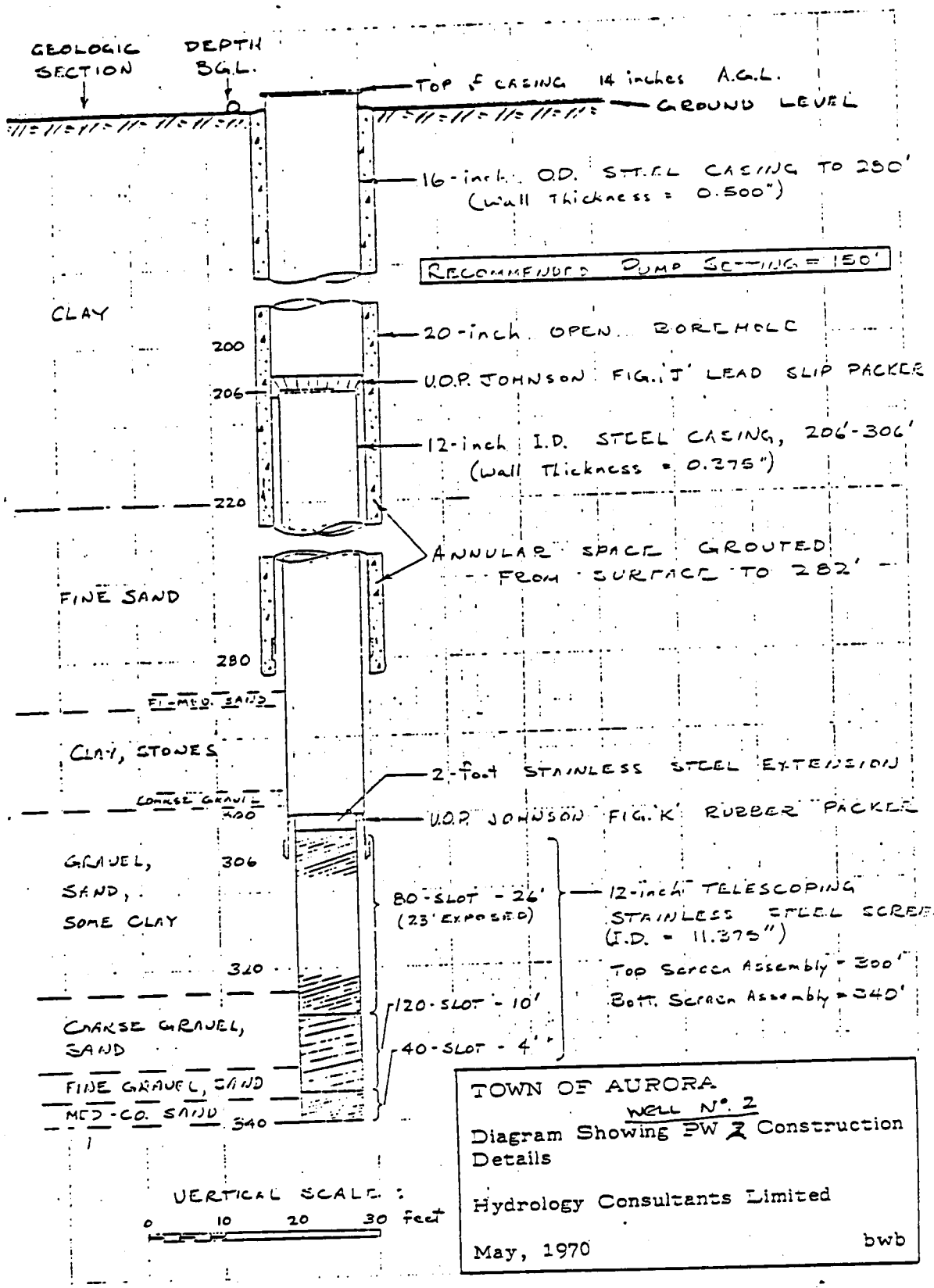
POLICE VILLAGE OF OAK RIDGES

DATE 8/1/67	SCALE 1:60	DRAWING NO.
BY GWM		

:ked

REMARKS

2


GEOLOGIC SECTION
DEPTH B.G.L.
TOP OF CASING 14 inches A.G.L.
GROUND LEVEL
16-inch O.D. STEEL CASING TO 280'
(Wall Thickness = 0.500")
RECOMMENDED PUMP SETTING = 150'
CLAY
200
20-inch OPEN BOREHOLE
206
U.O.P. JOHNSON FIG. 'J' LEAD SLIP PACKER
12-inch I.D. STEEL CASING, 206'-306'
(Wall Thickness = 0.375")
220
ANNULAR SPACE GROUTED
FROM SURFACE TO 282'
FINE SAND
280
FI-MED. SAND
CLAY, STONES
2-foot STAINLESS STEEL EXTENSION
COARSE GRAVEL
290
U.O.P. JOHNSON FIG. 'K' RUBBER PACKER
GRAVEL,
SAND,
SOME CLAY
306
80-SLOT - 24'
(23' EXPOSED)
12-inch TELESCOPING
STAINLESS STEEL SCREEN
(I.D. = 11.375")
Top Screen Assembly = 300'
Bott. Screen Assembly = 340'
320
120-SLOT - 10'
COARSE GRAVEL,
SAND
40-SLOT - 4'
FINE GRAVEL, SAND
MED-CO. SAND
340
VERTICAL SCALE :
0 10 20 30 feet
TOWN OF AURORA
WELL N°. 2
Diagram Showing PW 2 Construction Details
Hydrology Consultants Limited
May, 1970
bwb

VITA

Brett Whitney Frazier was born in Kingsport, Tennessee on November 6, 1962. He attended Holston Junior High and Elementary School and graduated from Sullivan Central High School as student body president in June 1981. The following September he entered the University of Tennessee, Knoxville, and received a Bachelor of Arts degree in Geology in December 1985. In January 1986, he accepted a research assistantship at the same university and began study toward a Master's degree in Environmental Engineering. During his study, he also accepted a teaching assistantship and a graduate assistantship. The Master's degree was awarded in December 1988.

The author is a member of the American Society of Civil Engineers and the American Water Works Association. After graduation, the author will pursue another Bachelor's degree in Civil Engineering.