

# Removal of Iron from Ground Water by Filtration

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THE most common method of removing iron from ground water involves three basic steps: aeration, detention, and filtration. Aeration introduces oxygen into the water to oxidize the ferrous iron. Detention provides time for the precipitation of iron, and in addition, effects some iron removal by settling. Filtration is relied upon to remove the rest of the iron. Problems have been encountered in the removal of iron by this method. In some waters it is difficult to oxidize ferrous iron completely, whereas in others a satisfactory iron precipitate cannot be formed.<sup>1-3</sup>

### Depletion of Oxygen

It has been observed that in some iron removal plants, reduction of iron from the ferric to the ferrous state occurred during filtration.<sup>4</sup> The reduction was always associated with a marked depletion of dissolved oxygen (DO) in the filter effluent. It was hypothesized that the depletion of DO was due to the biologic growth that occurs in filters. This could contribute to the development of an anaerobic and reducing environment in a conventional rapid sand filter. In natural waters containing ammonia, microbial ni-

trification would not only exert an oxygen demand, but might also cause a decrease in the pH of the water. Thus, low pH values and reducing conditions in a filter may alter chemical equilibrium, and as a result, precipitated iron may return to solution.

The current study was made using natural waters to determine the influence of biochemical and chemical changes on the removal of iron during filtration. It was conducted using a pilot plant, and was carried out at Clinton, Ill., where problems have been encountered in removing iron. Another purpose of the study was to determine remedial measures for plants which are ineffective in their operation.

### Equipment

A continuous flow pilot plant designed as an integrated series of unit operations was used for the study. Rubber, glass, and transparent rigid plastics were used to construct the apparatus to guard against any contact between water and iron. The apparatus was made so that it could be easily disassembled and transported for field studies. The plant was comprised of the following units:

1. Constant-flow head regulator
2. Aerator
3. Reaction-sedimentation basin
4. A bank of four rapid sand filters with different depths of filtering medium.

Figure 1 is a schematic flow diagram of the assembled pilot plant. Stands, supports, and accessories were used to obtain gravity flow. Pumping was necessary only for chemicals that were added directly to the reaction-sedimentation tank or to the filters. The well pump at Clinton was used to supply raw water to the pilot plant. All components of the pilot plant were designed to enable operation of four filters at 2 gpm/sq ft.

### Procedure

Aeration was accomplished by using diffused air in a multiple-pass aerator similar to that used by Lindenberg.<sup>5</sup> The circular aeration unit consisted of a 2-in. diameter central tube, a 3-in. diameter barrier tube, and a 6-in. diameter tube for the outside wall. Air was applied through a 2-in. diameter carborundum diffuser located at the bottom of the central tube. Raw water was introduced into the aerator through a nozzle in the center of the diffuser. The volume of the aerator was 6 liters. With a water flow rate of 0.40 gpm required to supply the four filters at 2 gpm/sq ft, the theoretical detention time in the aerator was 4 min. The air flow rate was adjusted to obtain a dissolved oxygen concentration of 6.5 to 8 mg/l in the aerated water.

The reaction basin had the dual purpose of providing detention to allow for the precipitation of iron and sedimentation. It was designed with a length-to-width ratio of 2:1 and the detention time provided was 60 min at a flow rate of 0.40 gpm. Tracer studies indicated

that the actual detention time provided by the tank at this flow rate was 48 min. A plastic tube with 0.125-in. diameter holes distributed the inflow downward and across the full width of the tank, at a submergence of about 16 in.

From the reaction basin, the water passed through a distribution box onto the filters. The rapid sand filters, each with a design loading of 2 gpm/sq ft, were 3-in. diameter transparent plastic tubes. The filter medium was screened sharp-grained sand having a grain size of 0.51 mm and a uniformity coefficient of 1.40. The depths of the sand beds in the four filters were 3, 9, 18, and 30 in. Filter backwashing was accomplished with treated plant water through a connection at the bottom of each filter. With a backwash rate of 10–12 gpm/sq ft, a bed expansion of about 50 per cent could be obtained.

The effluent from each filter passed into a float operated rate-of-flow controlling device. The controller maintained a constant rate of filtration of 2 gpm/sq ft, by maintaining a constant head on a  $\frac{1}{2}$ -in. needle valve. The float mechanism consisted of a 4-in. diameter copper float with a  $\frac{3}{4}$ -in. inlet valve. Each float chamber was made of transparent plastic and had dimensions of 9 by 9 by 15 in.

### Analytic Methods

At various stages of treatment analyses were performed for alkalinity, hardness, pH, oxidation-reduction potential (ORP), temperature, total dissolved solids, chlorides, nitrates, nitrites, ammonia, total iron, filterable and total ferrous iron, dissolved oxygen, chemical oxygen demand, organic nitrogen, bacterial count and chlorine demand. All analyses were performed

as per *Standard Methods*,<sup>6</sup> except for the two forms of ferrous iron and ORP.

Considerable uncertainty exists in the analytical determination of ferrous iron in the presence of ferric iron. The

Therefore, filterable ferrous iron must be distinguished from precipitated ferrous iron in studies of filtration. Filterable ferrous iron was determined in samples which had been filtered through 0.45- $\mu$  membrane filters.

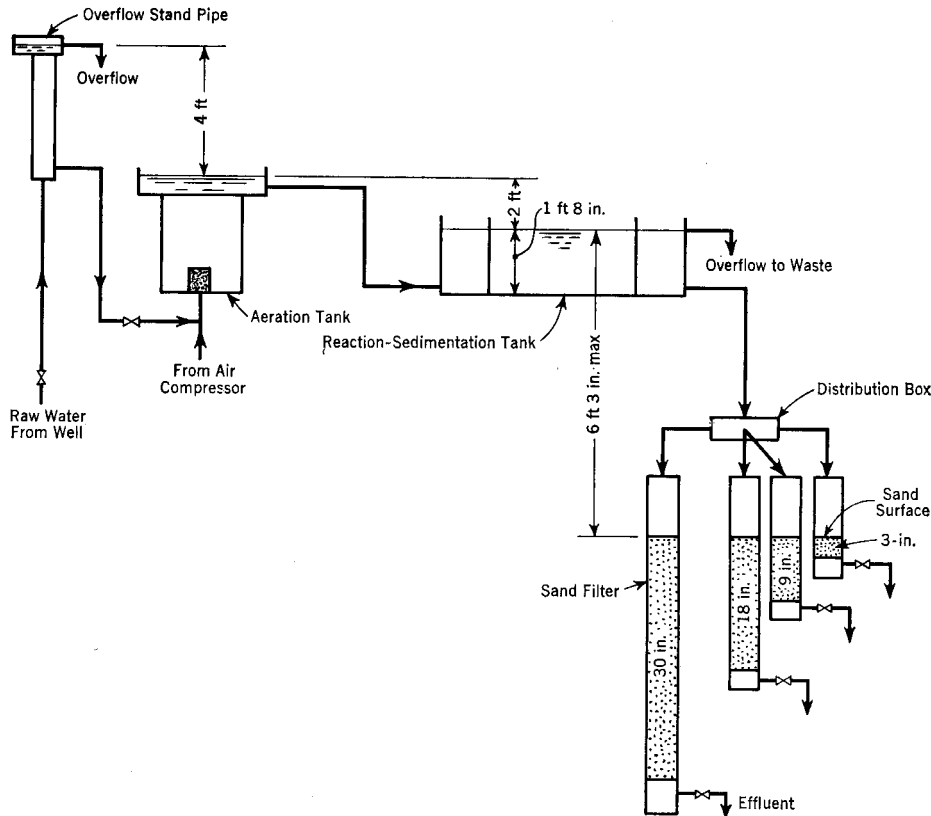


Fig. 1. Schematic Flow Diagram of Pilot Plant

*This pilot plant was designed especially for this study. The apparatus was made so that it could be easily disassembled and transported for field studies.*

method used for the present study was a modification of the method suggested by Lee and Stumm.<sup>7</sup> The modification was found necessary as demonstrated by the authors that in waters of high alkalinity, ferrous iron can precipitate as insoluble ferrous carbonate ( $\text{FeCO}_3$ ).<sup>8</sup>

#### Operation of Pilot Plant

The pilot plant was operated continuously during May through September 1963-65 at well No. 6 at Clinton.

During the first 8-10 weeks of operation, the pilot plant operated satisfac-

torily and produced water of acceptable quality. Afterwards, considerable slime growth was observed in the filters, oxygen was being depleted in the filter influent as it passed through, and ferrous iron was found in the filtered water in large amounts. The filters were backwashed at 48-hr intervals. Usually, the head loss in the filters immediately before backwash was about 5 ft. It was observed that even with a backwash rate as high as 12 gpm/sq ft, it was not possible to wash all the slime growth off the filtering medium. Using the "ripened" filters, studies were made to determine the pattern of iron breakthrough and to observe the influence of biologic growth during the filtration period. Samples were taken at different locations in the pilot plant at regular intervals (4-6 hr) during a filtration period. Occasionally, sand samples at depths of 0.25, 3, 9, and 30 in., and backwash waters from the filters were collected and analyzed for iron, COD, and organic nitrogen.

When nitrification was evident in the deeper ripened filters, the second phase of the study was initiated by adding a specific inhibitor, thiourea, to the filter influent, in an effort to control the activity of the nitrite-forming bacteria (*nitrosomonas*). This was followed by a study of the inhibition of all bacterial growth using a general inhibitor.\* These inhibition studies were undertaken to determine whether anaerobic conditions and the passage of iron through the filters were closely related and biologically mediated. Finally, a preliminary study of inhibition with chlorine was made.

\*"Roccal," a product of Winthrop Lab., New York. Active ingredient: Alkyl-dimethylbenzylammonium chloride (10 per cent). Inert ingredient: water (90 per cent).

### Unripened Filters

Studies conducted during the summers of 1963-65 indicated that 8-10 weeks would elapse before reducing conditions developed in the new, clean experimental filters. This was considered the ripening period. Studies made prior to ripening were devoted mainly to the determination of the pattern of iron breakthrough in filters

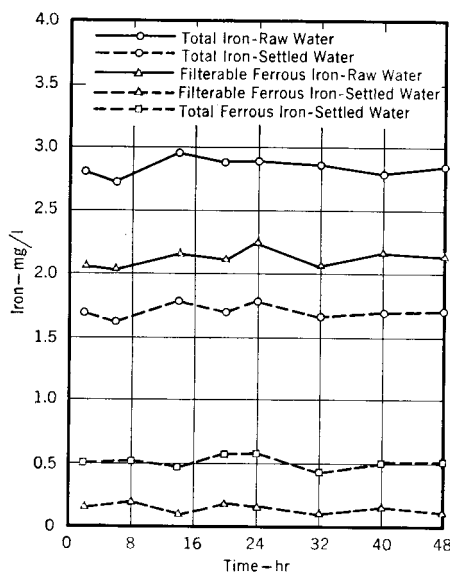
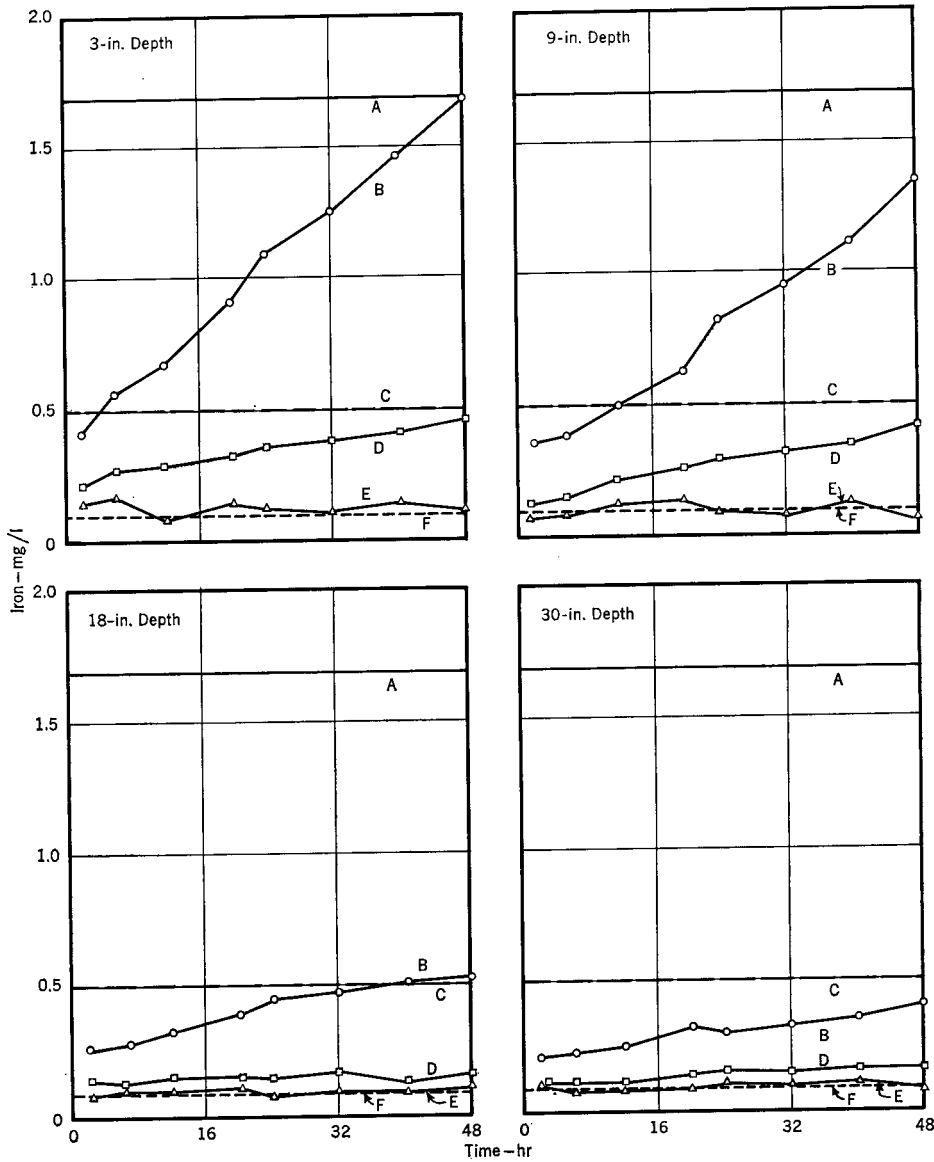


Fig. 2. Iron Concentration in Raw and Settled Water

*Aeration and detention partially oxidized and precipitated the ferrous iron in the raw water.*

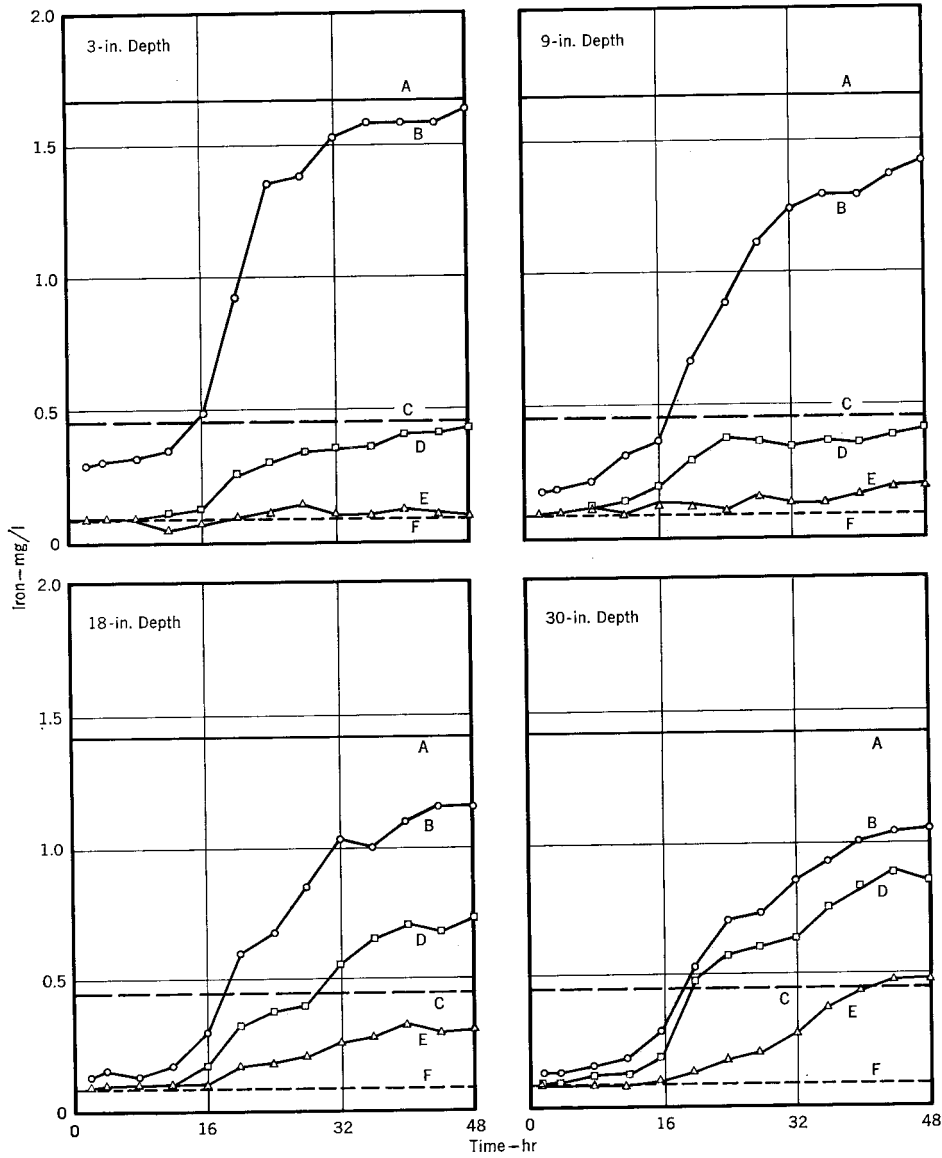
which had a relatively small amount of biologic growth and were operating normally.

Measured characteristics of the raw and settled water during a typical experiment are shown in Table 1. It can be seen that there was an increase of about 0.3 units in the pH value of the water following aeration and settling.



**Fig. 3. Iron Concentration in Filtered Water**

*A—Average influent total iron; B—Total iron; C—Average influent ferrous iron; D—Total ferrous iron; E—Filterable ferrous iron; F—Average influent filterable ferrous iron. Only the 30-in. filter reduced the total iron to an acceptable level.*



**Fig. 4. Iron Concentration in Filtered Water**

*A—Average influent total iron; B—Total iron; C—Average influent ferrous iron; D—Total ferrous iron; E—Filterable ferrous iron; F—Average influent filterable ferrous iron. After 16–18 hr of filtration, the filterable ferrous iron in the effluent from the 18 and 30 in. filters was higher than that present in the influent.*

TABLE 1  
 Characteristics of Raw and Settled Water

Sample Type	Time hr	DO, mg/l	pH	ORP, mv	Alkalinity, mg/l as CaCO <sub>3</sub>	Total Hardness, mg/l as CaCO <sub>3</sub>	Ca Hardness, mg/l as CaCO <sub>3</sub>	Org.-N, mg/l	NH <sub>4</sub> -N, mg/l	COD, mg/l	Bacteria Count, no./ml
Raw	2	0	7.25	+330	440	343	180	3.5	3.2	34	160
	6	0	7.30	+322	—	—	—	—	—	—	—
	12	0	7.31	+317	—	—	—	3.8	2.9	32	280
	20	0	7.27	+328	—	—	—	—	—	—	—
	24	0	7.28	+325	428	350	184	—	—	—	—
	32	0	7.22	+328	—	—	—	2.9	3.0	35	210
	40	0	7.31	+332	—	—	—	—	—	—	—
	48	0	7.32	+330	434	338	172	3.1	3.1	35	120
Aerated and Settled	2	7.2	7.75	+440	424	328	171	3.6	3.2	25	1,700
	6	7.1	7.68	+432	—	—	—	—	—	—	—
	12	6.8	7.70	+428	—	—	—	3.7	3.0	22	2,200
	20	6.8	7.62	+445	—	—	—	—	—	—	—
	24	6.7	7.58	+418	396	331	173	—	—	—	—
	32	7.3	7.56	+429	—	—	—	3.1	2.8	29	3,100
	40	6.9	7.67	+413	—	—	—	—	—	—	—
	48	7.7	7.55	+438	418	317	161	3.0	2.9	31	2,600

This was due to the stripping of carbon dioxide ( $\text{CO}_2$ ) from the water. The increase in pH was accompanied by a decrease in alkalinity and hardness, apparently due to the precipitation of carbonate hardness.

Bacterial counts were made using nutrient agar plates incubated for 48 hr at 25°C. Therefore, the bacterial counts indicated in Table 1 do not include nitrifying organisms which cannot grow on nutrient agar. There was no evidence of nitrification in the effluent from the settling tank.

measured ORP value of the water following the introduction of oxygen.

Figure 2 shows the concentrations of different forms of iron in raw and settled water as recorded during the period covered in Table 1. No ferrous iron precipitate was found in the raw water. However, the average concentration of filterable ferrous iron in the raw water was almost 75 per cent of the total iron. In the filter influent, after aeration and detention, the average filterable ferrous iron concentration

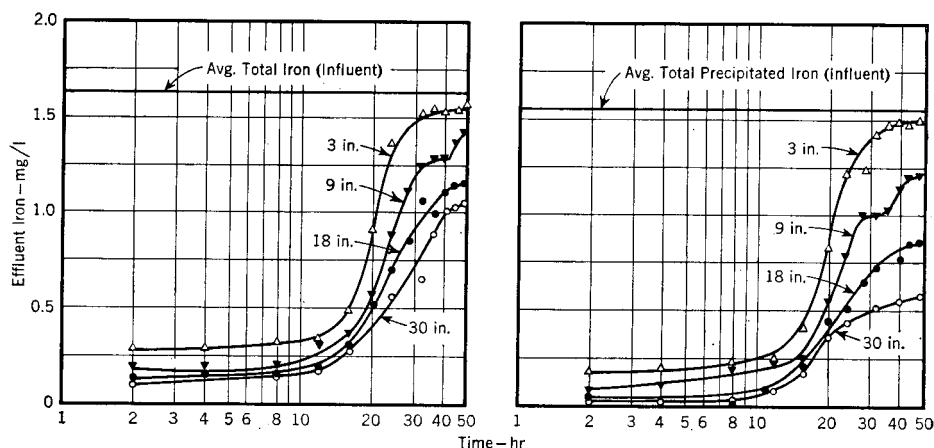


Fig. 5. Breakthrough of Iron in Ripened Filters

*The ripened filters were at least as effective as the unripened filters for up to 16 hr.*

Although the raw water was totally devoid of oxygen, the aeration device introduced between 6.5 and 7.8 mg/l of DO. There was a small decrease in the DO concentration during settling (0.5–0.8 mg/l). This was believed to be caused by the oxygen demand exerted by the microorganisms and the oxidation of ferrous iron in the settling tank. There was also a consistent increase of about 100 mv in the

was less than 10 per cent of the total iron, while the total ferrous iron concentration in the filter influent was 30 per cent. In other words, 20 per cent of the total iron present in the settled water was ferrous iron, which was either insoluble or may have been adsorbed on the insoluble ferric oxide hydrates. Only 40 per cent of the total iron in the raw water was removed by aeration and settling.

TABLE 2  
 Characteristics of Filtered Water

Depth, <i>in.</i>	Time, <i>hr</i>	DO, <i>mg/l</i>	pH	ORP, <i>mv</i>	Alkalinity, <i>mg/l as CaCO<sub>3</sub></i>	Total Hardness, <i>mg/l as CaCO<sub>3</sub></i>	Ca Hardness, <i>mg/l as CaCO<sub>3</sub></i>	Nitrogen— <i>mg/l</i>		COD, <i>mg/l</i>	Bacteria Count, <i>no./ml</i>
								Organic	Ammonia		
3	2	6.5	7.80	+442	410	331	172	2.7	3.2	20.1	1,730
	12	6.3	7.70	+452	—	—	—	2.5	3.0	22.0	2,800
	20	6.4	7.62	+453	—	—	—	—	—	—	—
	24	6.2	7.55	+445	388	342	181	—	—	—	—
	32	6.5	7.58	+457	—	—	—	3.5	3.2	28.0	7,200
	40	6.8	7.65	+462	—	—	—	—	—	—	—
	48	7.1	7.53	+453	412	327	165	4.1	3.1	32.0	7,800
9	2	6.3	7.70	+440	410	315	162	1.2	2.8	7.0	560
	12	6.4	7.71	+458	—	—	—	1.3	—	18.2	1,250
	20	6.0	7.63	+453	—	—	—	—	2.8	—	—
	24	6.1	7.54	+455	386	324	178	—	—	—	—
	32	6.2	7.41	+463	—	—	—	2.0	3.2	20.8	1,800
	40	6.3	7.53	+453	—	—	—	—	—	—	—
	48	6.4	7.58	+453	410	306	163	—	3.1	21.3	2,300
18	2	6.2	7.65	+438	408	312	158	1.0	2.8	6.5	430
	12	6.1	7.62	+465	—	—	—	1.2	2.9	17.2	1,120
	20	6.0	7.58	+468	—	—	—	—	—	—	—
	24	5.9	7.53	+472	386	318	165	1.8	3.1	20.2	1,700
	32	6.0	7.43	+461	—	—	—	—	—	—	—
	40	6.1	7.50	+478	—	—	—	—	—	—	—
	48	5.8	7.57	+474	410	304	163	1.9	3.2	21.1	1,850
30	2	6.1	7.53	+448	402	310	161	nil	3.0	6.4	440
	12	6.0	7.69	+463	—	—	—	1.1	—	8.7	960
	20	5.3	7.61	+478	—	—	—	—	—	—	—
	24	5.8	7.59	+463	384	310	175	1.3	2.8	17.0	1,130
	32	5.9	7.43	+458	—	—	—	—	—	—	—
	40	5.7	7.58	+468	—	—	—	—	—	—	—
	48	5.8	7.60	+460	408	296	160	1.7	3.0	20.0	1,620

### Analyzing Filtered Water

Figure 3 shows the concentration of iron in the filtered water. At depths of 3 and 9 in. a large amount of total iron passed through the filters. It continued to increase throughout the filtration period. After 48 hr, the amount of total iron almost equalled the amount in the influent. This was also true of the total ferrous iron. However, the concentration of ferrous iron in the filtered water was equal to that in the influent, and remained fairly constant during the filtration period. Only the 30-in. filter reduced the total iron to an acceptable level.

The characteristics of the filtered water with regard to DO, pH, ORP, alkalinity, and total hardness are shown in Table 2. The pH did not change significantly in any of the filters. However, a slight decrease in the DO concentration was observed as filter depth and time following backwash increased. In addition, there was a slight upward trend in the ORP values during filtration. As the influent water was apparently unstable, because it was supersaturated with calcium carbonate, the slight decrease in hardness with filter depth was taken as an indication of the precipitation of carbonate hardness in the filters. Overall, there was no substantial change in these characteristics as a result of filtration.

Table 3 shows the results of an analyses of the backwash waters at the conclusion of the filtration period. The precipitate recovered had a total ferrous iron fraction which varied from 9.1 to 19 per cent, depending on the depth of the filter. The greater the depth, the higher the degree of oxidation. No filterable ferrous iron could be found in the supernatant of centrifuged samples of the backwash water.

### Ripened Filters

After 8–10 weeks of filter operation, a significant depletion of dissolved oxygen was observed between the filter influent and effluent for all four filters. This was accompanied by the formation of nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ), slight decreases in pH, ORP, alkalinity, and a reduction of iron from the ferric to the ferrous state. A progressive buildup of bacteria was observed in the filter. The bacteria could not be washed off the sand grains even with prolonged backwashing.

The average quality of the raw water and filter influent, both aerated and settled, was much the same throughout

TABLE 3

*Analysis of Backwash Water at the Conclusion of a Filter Run*

Filter Depth in.	Ferrous Iron per cent	COD mg/l	Org-N mg/l	Bacteria Count, no./ml
3	19.0	17	1.2	6,300
9	16.7	25	1.8	11,300
18	9.8	33	2.1	12,800
30	9.1	42	3.2	16,200

the study. The results of iron analyses on the raw and settled water during a filtration period following the ripening of the filters were substantially the same as shown in Fig. 2.

Figure 4 shows the concentrations of the various forms of iron in the effluent from the ripened filters. The average influent iron concentrations are also indicated.

### Total Iron Breakthrough

A definite total iron breakthrough was evident in all the filters after 16 hr. In the case of the 3- and 9-in. filters, the iron was primarily ferric, whereas the 18- and 30-in. filters were

TABLE 4  
Correlation Between Nitrification and Oxygen Uptake in 30-in. Filter

Time hr	Nitrogen—mg/l						
	Ammonia-N influent avg. (1)	NO <sub>2</sub> <sup>-</sup> -N Formed (observed) (2)	NO <sub>3</sub> <sup>-</sup> -N Formed (observed) (3)	Ammonia-N Oxidized (computed) (4) = (2) + (3)	Ammonia-N Unoxidized (computed) (5) = (1) - (4)	Ammonia-N in Effluent (observed) (6)	Ammonia-N Utilized in Excess of Requirement for Nitrification (7) = (5) - (6)
2	2.95	0.09	0.44	0.53	2.42	1.92	0.50
8	2.95	0.29	0.88	1.17	1.78	0.98	0.80
16	2.95	0.35	1.01	1.36	1.59	0.71	0.88
24	2.95	0.20	1.08	1.28	1.67	0.44	1.23
32	2.95	nil	1.21	1.21	1.74	0.14	1.60
40	2.95	nil	1.23	1.23	1.72	nil	1.72
48	2.95	nil	1.26	1.26	1.69	nil	1.69

Time hr	Dissolved Oxygen—mg/l						
	Influent avg. (8)	For NO <sub>2</sub> <sup>-</sup> (computed) (9)	For NO <sub>3</sub> <sup>-</sup> (computed) (10)	Total Demand (computed) (11) = (9) + (10)	Remaining (computed) (12) = (8) - (11)	Effluent (observed) (13)	Balance (computed) (14) = (12) - (13)
2	7.0	0.31	2.00	2.31	4.69	3.4	1.29
8	7.0	0.99	4.00	4.99	2.01	1.2	0.81
16	7.0	1.20	4.60	5.80	1.20	0.2	1.00
24	7.0	0.68	4.90	5.58	1.42	nil	1.42
32	7.0	nil	5.50	5.50	1.50	nil	1.50
40	7.0	nil	5.60	5.60	1.40	nil	1.40
48	7.0	nil	5.72	5.72	1.28	nil	1.28

Column 7: The values represent the fraction of ammonia nitrogen that appeared to be synthesized into the bacterial cell mass.

Column 9: The values were computed using the equation:  $\text{NH}_4^+ + 1.5 \text{O}_2 = \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O}$ .

Column 10: The values were computed using the equation:  $\text{NH}_4^+ + 2 \text{O}_2 = \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$ .

Column 14: The values represent the amount of dissolved oxygen that appeared to be used for deriving energy for the species of aerobic bacteria other than the nitrifiers.

passing ferrous iron, largely in filterable form. The filterable ferrous iron concentration in the effluent from the 3-in. filters was not higher than that in the influent at any given time. On the other hand, as filtration progressed, there was a gradual increase in the concentration of filterable ferrous iron in the effluent from the 9-, 18-, and 30-in. filters. After 16–18 hr, the filterable ferrous iron concentration in the effluent from the 18- and 30-in. filters was higher than that present in the influent.

The total ferrous iron concentration (filterable ferrous plus precipitated or adsorbed ferrous iron) in the effluent from the 3- and 9-in. filters never exceeded that in the influent. However, after 20–30 hr, the total ferrous iron in the effluent from the 18- and 30-in. filters exceeded that in the influent. This was taken as an indication that a reduction of ferric iron to the ferrous state and partial precipitation as ferrous carbonate occurred in the filters.

The passage of iron precipitates through the filters may have been due to the colloidal nature of the insoluble species of iron. In view of the penetrating ability of such a colloid, a depth of filter medium less than 18 in. appears to be insufficient.

The typical pattern of the breakthrough of total iron and precipitated iron is illustrated in Fig. 5. It was observed that the ripened filters were at least as effective as the unripened filters (Fig. 3) in removing iron for up to 16 hr. In fact, it appeared that the ripened filters were more effective. This may have been because the sand grains of the ripened filters were coated with iron oxides and slime growths, which improved filtration efficiency. Some investigators have credited this increased efficiency of filtration in ripened filters to the phenomenon of

surface catalysis, which occurs when the sand grains are coated with iron oxides.<sup>9</sup> It is apparent that the breakthrough of iron in ripened filters is not experienced in the initial stages of filtration.

### Effect of Nitrification

In ripened filters it was observed that the concentration of ammonia nitrogen in the effluent decreased gradu-

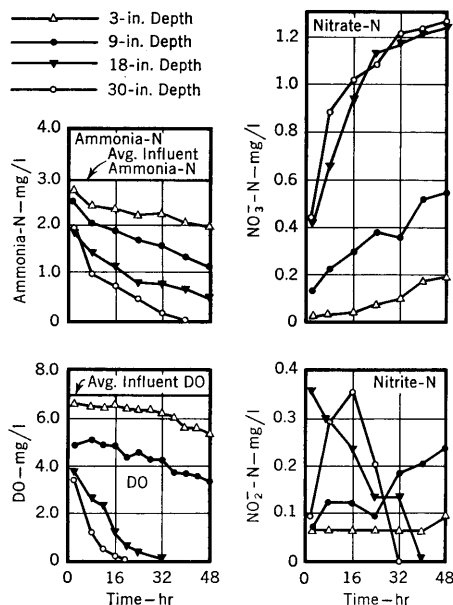


Fig. 6. Effect of Nitrification on Dissolved Oxygen Content of Filter Effluent

After 2 hr, half the influent dissolved oxygen was depleted in the 18- and 30-in. filters.

ally as time of filtration increased. The decrease in ammonia nitrogen was marked by a proportional increase in the nitrate nitrogen concentration. Simultaneously, there was a depletion of DO, a decrease in ORP and pH, and an increase in the concentration of iron.

Figure 6 shows the ammonia, nitrite, nitrate nitrogen, and the DO concen-

tration in the effluent from the filters. After 2 hr, half the influent DO was depleted in the 18- and 30-in filters. Prior to the attainment of terminal head loss, the effluents from these filters were completely devoid of DO. From Fig. 4, it can be seen that, at about the same time the DO was depleted, there was an apparent reduction of iron from the ferric to the ferrous state.

The DO content of the effluents from 3- and 9-in. filters was 5.5 and 3.4 mg/l after 48 hr. No reduction of iron from ferric to ferrous form was observed in either of these filters.

concomitant increase in the concentration of nitrate nitrogen in the effluent as shown in the same figure. The degree of nitrification was least in the 3-in. filter and greatest in the 30-in. filter.

### Nitrification and D.O. Depletion

The correlation between the degree of nitrification and the indicated amount of DO depletion in the 30-in. filter is shown in Table 4. The values for the oxygen utilized in the formation of nitrite and nitrate from ammonia were computed from the ob-

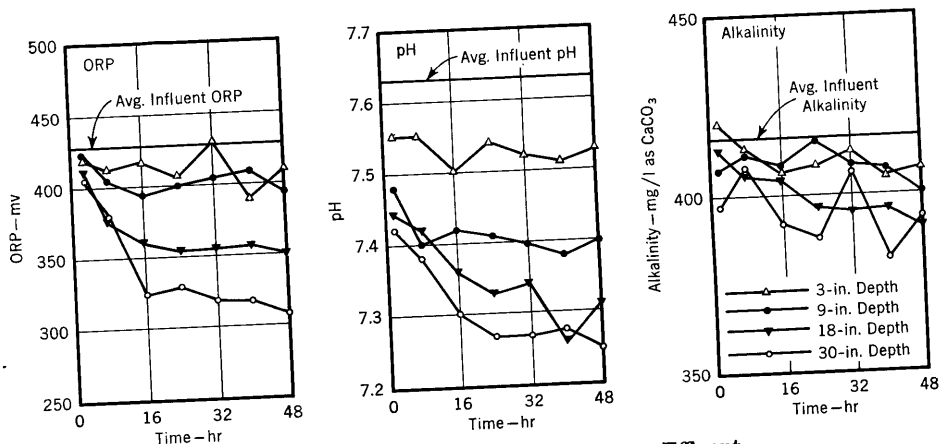


Fig. 7. Alkalinity, pH, and ORP of Filter Effluent

*There were measurable changes in the 18- and 30-in. filters.*

The ammonia nitrogen concentration in the effluent from all filters decreased gradually with increasing time of filtration. The effluent ammonia nitrogen content indicated a depletion of approximately 1, 2, 2.5, and 3 mg/l for the 3-, 9-, 18-, and 30-in. filters, after a 48-hr filtration period. A correlation between the depletion of DO and ammonia nitrogen is apparent. The depletion of the ammonia nitrogen and DO concentrations was marked by a

served concentration of nitrite and nitrate using the equations listed in Table 4. The amount of ammonia nitrogen oxidized at any given time was estimated from the observed values for the nitrite and nitrate nitrogen. Thus, it was possible to estimate the unoxidized fraction of the ammonia nitrogen. By subtracting the computed values for the ammonia nitrogen residuals from the corresponding observed residual values, the fraction of ammonia nitro-

gen that was utilized in excess of the requirement for nitrification may be estimated. This may have been synthesized into cell material. It is shown in Column 7. Slowly, at first, then more rapidly after 16 hr, this fraction increased, indicating the possibility of an increase in the bacterial population with time of filtration.

By subtracting the observed residual values of DO from the computed ones, it was possible to determine the amount of DO that may have been utilized by the species of aerobes other than the nitrifiers for the energy-yielding oxidation processes. These results are

a similar observation in his investigation on biologically mediated corrosion of iron. Such acid-producing reactions may lead to a decrease in alkalinity resulting in a solution of precipitated ferrous iron or the desorption of adsorbed ferrous iron.

Figure 7 shows the change in pH, ORP, and alkalinity values in the filter effluents. No appreciable change in pH and alkalinity values was observed in the 3-in. filter, because there was no significant nitrification in this filter. However, in the 18- and 30-in. filters, there was a measurable decrease in pH and alkalinity.

TABLE 5  
*Sand Analysis*

Depth <i>in.</i>	Iron <i>mg/gm of sand</i>		Ferrous Iron <i>per cent</i>	COD <i>mg/gm of sand</i>	Organic-N <i>mg/gm of sand</i>	Bacteria count, <i>no./mg of sand</i>
	Total	Total Ferrous				
0.25	37.8	3.9	10.3	182.0	18.7	380,000
3	23.2	2.5	10.6	65.0	6.4	93,000
9	16.7	2.6	15.4	18.5	1.8	12,500
18	14.6	3.7	25.5	8.3	0.6	3,800
30	12.3	3.6	28.9	4.5	0.4	2,400

shown in Column 14. This value was fairly constant during the filtration period. From these computations, it appeared that there was a relationship between the amount of ammonia oxidized, the amount of DO depleted, and the amount of oxidized nitrogen compound.

#### Effect on pH and Alkalinity

An important aspect of microbial nitrification, which may play a significant role in changing the chemical environment within a filter, is the production of H<sup>+</sup> ions, as illustrated by the equations in Table 4. Larson<sup>10</sup> made

There was little change in the ORP value of the effluent from the 3- and 9-in. filters as compared to the influent. However, the effluent from the 18- and 30-in. filters exhibited an appreciable decrease in ORP during filtration. The depletion of dissolved oxygen in these filters (Fig. 6) was associated with this marked decrease in ORP.

#### Biologic Growth During Filtration

The concentration of COD and organic nitrogen is shown in Fig. 8. Figure 9 shows the bacterial count. The COD and organic nitrogen contents of the effluent were generally less

than that of the influent. No appreciable amounts of COD or organic nitrogen were found in the supernatant of centrifuged effluent samples. However, as indicated in Table 1, the influent contained appreciable amounts of COD and organic nitrogen. These results were taken as an indication that soluble COD and organic nitrogen were being utilized for bacterial growth and that the bacteria initially remained in the filters.

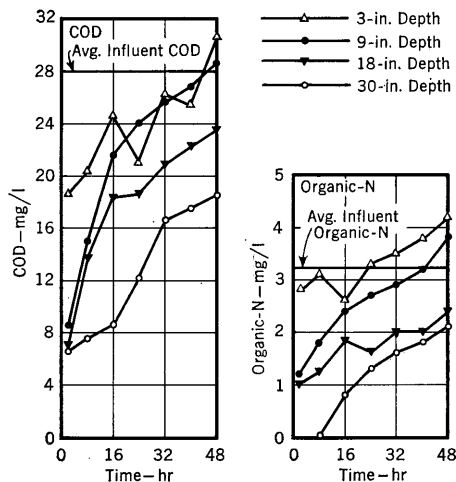


Fig. 8. COD and Organic Nitrogen in Filter Effluent

*COD and organic nitrogen in the effluent increased with time of filtration.*

The COD and organic nitrogen increased with time of filtration. This may have been due to the filters passing an increasing number of bacteria as they became clogged. The amount of COD, organic nitrogen and the number of bacteria being passed by a filter usually depended upon filter depth. The deeper filters passed lesser amounts of each.

An analysis of sand samples at various depths of the 30-in. filter is shown

in Table 5. The data were collected at the conclusion of the last experiment performed during 1964. In deeper sections, a large fraction of the precipitated iron was in ferrous form. The ferrous iron may have been either insoluble or adsorbed by the ferric hydrates. The percentage of ferrous iron in the precipitate was found to vary from 10 near the surface of the filter to 29 at the bottom. The organic nitrogen and COD data followed the same trend as the bacterial count.

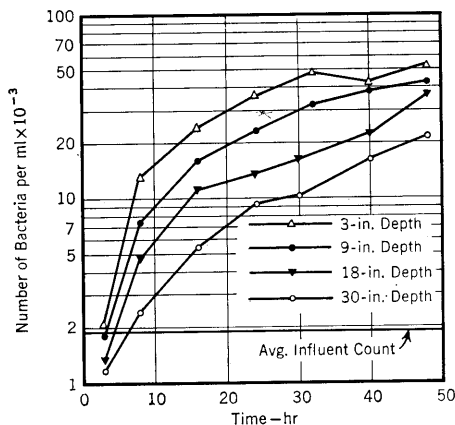


Fig. 9. Bacterial Count in the Effluent

*The bacterial population in the effluent also increased with time of filtration.*

These three values were highest at the filter surface.

**Inhibition Studies**

As the ripened filters showed evidence of nitrification, attempts were made to maintain aerobic conditions by inhibiting the growth of the nitrite-forming bacterium, *nitrosomonas*. Two 30-in. filters were employed. One, referred to as the "control" hereafter, was continuously fed a dose of the inhibitor throughout the duration of the

experiment. The other 30-in. filter was allowed to ripen before the inhibitor was added.

Thiourea has been extensively used as an inhibitor for *nitrosomonas*.<sup>11, 12</sup> Three dosages of thiourea were used in the study, namely,  $10^{-5}$ ,  $5 \times 10^{-5}$ , and  $10^{-4}$  M in three different experiments. With  $10^{-4}$  M, nitrification did not occur. Nitrification could also be eliminated in the ripened filters after 24 hr of continuous feeding of thiourea at a rate of 7.6 mg/l ( $10^{-4}$  M). Figure 10 shows the results of the experiment where thiourea was fed at a dose of 7.6 mg/l ( $10^{-4}$  M) to both filters. The concentration of iron being passed by the ripened filter prior to the addition of inhibitor is shown in Fig. 10a. The same figure also shows the effluent iron concentrations from the control (Fig. 10c), and the ripened filter (Fig. 10b) after it was treated with thiourea for 24 hr. Comparing the control (Fig. 10c) and the treated ripened filter (Fig. 10b), it is apparent that both performed with equal efficiency. There was no reduction of ferric iron to the ferrous form and no appreciable increase in the soluble ferrous iron content in the effluent from either of the filters when the inhibitor was fed to the filter influent.

In comparing the quality of the effluent from both the control and the ripened filter dosed with thiourea, the data indicated that no nitrification occurred in either of the filters. There was a slight increase in the organic nitrogen content in the effluent from both filters toward the end of the experiment. This may have been due to the organic nitrogen contributed by the addition of thiourea. The bacterial count in both effluents was rather high. This suggested that thiourea did not inhibit the growth of bacterial species

other than *nitrosomonas*. Dissolved oxygen was not depleted during filtration, nor did the pH and ORP values of the water change significantly. The experimental results are shown in Table 6.

### Chlorination of the Influent

In an effort to find an economical and practical measure to improve conditions in ripened filters, preliminary investigations of chlorination of the influent prior to filtration were carried out. Once again, the investigation was carried out on two 30-in. filters, one of which was used as a control.

One of the filters was allowed to ripen. When reducing conditions developed, chlorination was initiated. The control in this case was a new filter which was not placed in service until reducing conditions were evident in the ripened filter. Three different chlorine doses, 5, 8, and 50 mg/l, were used for both the control and the ripened filters in three different experiments. It was observed that a chlorine residual of 0.2 mg/l could be maintained through the control filter at a dosage of 8 mg/l. However, at this dosage no residual chlorine could be maintained in the effluent from the ripened filter. Nitrification could not be completely inhibited in either of the filters at a chlorine dosage of 8 mg/l. This may have been due to the fact that the ammonia present in the water could not be completely oxidized by this dosage of chlorine. This was indicated by the presence of ammonia in the effluent. Therefore, superchlorination with a dosage of 50 mg/l was undertaken to oxidize all the ammonia present in order to inhibit the energy-yielding reactions for the growth of *nitrosomonas*. As expected, nitrification

TABLE 6  
Quality of Filtered Water With Addition of Thiourea

30-in. Filter	Time hr	DO mg/l	pH	E <sub>h</sub> mv	Alkalinity mg/l as CaCO <sub>3</sub>	Nitrogen—mg/l				COD mg/l	Bacteria Count no./ml
						Organic	Ammonia	Nitrite	Nitrate		
Control	2	7.0	7.69	+440	420	1.7	2.4	nil	nil	7.0	920
	8	6.8	7.72	+442	413	2.6	2.9	nil	nil	6.8	1,300
	16	7.1	7.70	+452	427	3.0	2.8	nil	nil	8.8	5,600
	24	6.7	7.63	+432	426	3.3	2.9	nil	nil	14.0	12,000
	32	6.9	7.67	+445	432	3.8	3.1	nil	nil	16.0	15,000
	40	6.8	7.58	+425	423	4.2	2.7	nil	nil	18.3	18,000
	48	6.8	7.62	+428	418	4.3	4.0	nil	nil	24.3	23,000
	Ripened	2	6.5	7.70	+456	426	1.6	2.9	nil	nil	5.6
8		6.8	7.70	+434	422	1.4	2.8	nil	nil	7.5	1,700
16		7.0	7.70	+442	420	2.8	2.3	nil	nil	7.2	7,200
24		6.3	7.76	+438	413	4.1	3.0	nil	nil	9.3	9,000
32		6.4	7.60	+430	430	3.6	2.5	nil	nil	10.2	12,500
40		6.2	7.63	+417	428	4.0	2.7	nil	nil	13.2	13,000
48		6.6	7.68	+436	416	4.3	.8	nil	nil	18.6	19,000

could be completely stopped at this dosage, and a substantial chlorine residual could be maintained in the effluent from the filter. In addition, there was no reduction of iron from the ferric to the ferrous state.

### Conclusions

In pilot plant studies of iron removal using a well water source from Clinton, Ill., it was found that it was possible by aeration and detention to convert

of iron is quite satisfactory. The degree of removal depends on the depth of the filtering medium. In addition, there is evidence of some oxidation of ferrous iron within the filters.

After a period of 8–10 weeks of continuous operation, there is extensive biologic growth in the filters. The concentration of dissolved oxygen is reduced during filtration especially with filter depths of 18 in. or more. There is also a significant decrease in pH and

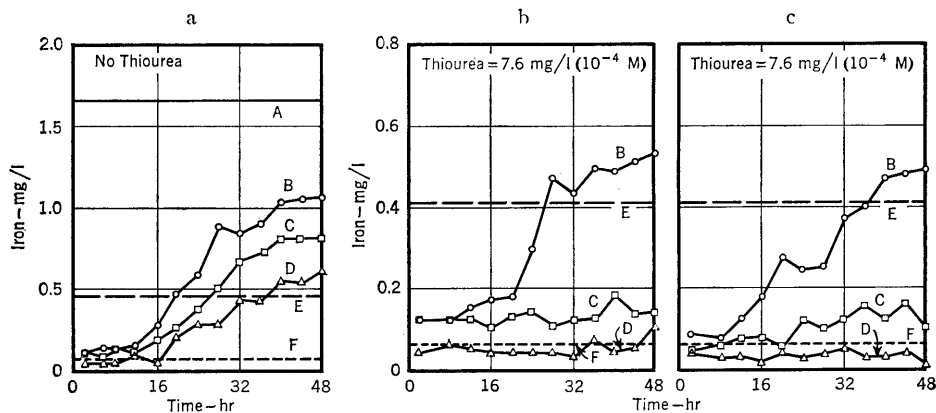


Fig. 10. Improvement of Iron Removal Efficiency by Inhibition of Nitrification

*Inhibition of nitrification with thiourea eliminated the reduction of ferric iron in the filter and restored the efficiency of filter operation.*

the soluble ferrous iron in the raw water to either the ferric or an insoluble ferrous state, presumably  $\text{FeCO}_3$ . Complete oxidation of the ferrous iron did not occur even with DO concentrations near the saturation level. It is possible, however, that a fraction of the ferrous iron may have been adsorbed on the ferric hydrate precipitates.

Under conditions of pilot plant operation, when the concentration of DO can be maintained in the effluent from the filter and there is no extensive biologic growth in the filter, the removal

ORP. In addition, there is evidence of nitrification in the filters.

In ripened filters undergoing nitrification, iron was reduced from the ferric to the ferrous state at approximately the same time that the concentration of DO was totally depleted. At such times, filters having depths of 18 in. or more, passed large amounts of iron, much of which was in the ferrous state. A large fraction of the ferrous iron being passed by the filters was capable of passing a  $0.45\text{-}\mu$  membrane filter. Reducing conditions were not observed in the 3- or 9-in. filters. The

dissolved oxygen was not totally depleted at these depths. Most of the iron passed in the effluent from the 9-in. filter was in the ferric form.

It appeared that in a ripened filter the aerobic species of bacteria, including the nitrifiers, predominated. With increasing filtration time there was an increase in the bacterial population in the filters. Ultimately, the oxygen demand imposed by the growing aerobic population exceeded the DO content of the influent. It is believed that this led to reducing conditions in the 18- and 30-in. filters which was then responsible for the reduction of iron from the ferric to the ferrous state.

Nitrification in a filter was effectively eliminated by using thiourea for *nitrosomonas*, at a rate of 7.6 mg/l ( $10^{-4}$  M). It was possible to restore a ripened filter to normal efficiency provided a continuous feed of the inhibitor was maintained. By inhibiting nitrification, it was possible to maintain aerobic conditions in a filter and thus prevent the reduction of iron from the ferric to the ferrous state.

Preliminary investigations with pre-chlorination, indicated that nitrification cannot be inhibited in a 30-in. filter unless the chlorine dosage approaches the stoichiometric requirement for oxidation of the ammonia present. However, occasional superchlorination of the filters during backwash, followed by a continuous chlorine feed may satisfactorily control biologic growth in the filter and prevent reduction of iron from the ferric to the ferrous state.

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