REMOVAL OF NITRATES FROM WATER
BY
CHEMICAL REDUCTION

by

George Kenneth Young, Jr.

Thesis submitted to the Graduate Faculty of the

Virginia Polytechnic Institute

in candidacy for the degree of

MASTER OF SCIENCE

in

Sanitary Engineering

August, 1962

Blacksburg, Virginia

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I. INTRODUCTION

The consumption of water having a high concentration of nitrate ion or of milk formulas using such water is reported to be the cause of "blue babies", a condition known as "ideopathic" methemoglobinemia. The nitrates are reduced to nitrites in the digestive system, and enter the blood stream to unite with red corpuscles, resulting in discoloration of the red blood cells and in interference with oxygen transfer capacity. This condition may cause death of very small infants; but in many instances, cures are achieved by substituting nitrate-free water(1) .

The current (1961) U. S. Public Health Service drinking water standards specify an upper level of nitrate of 45 mg./l. (as nitrate), with higher nitrate levels considered unsafe(2) .

Nitrates find their way into drinking water via: industrial wastes (explosives, fertilizer, and other nitration processes), use of nitrates to maintain aerobism in streams and lagoons, ground water leaching of fertilized fields, municipal sewage disposal processes with nitrate as an end product, and mineral salts leached from the earth's crust. Considering the current and future degree of water reuse, it is evident that nitrate levels in drinking water will increase.

At present the nitrate health hazard is restricted to rural well supplies in the western portion of the United States and to localities downstream from plants discharging nitrates in industrial wastes. As nitrate contamination of water increases, large scale industrial and municipal nitrate removal methods may become necessary.

Any of the desalination techniques currently under investigation for sea water or brackish water could be used for removing nitrate. Unfortunately, these processes of ion-exchange, electrodialysis, distillation, and freezing seem far too expensive for common water supplies such as lakes, streams, and wells. Removal of nitrate from sewage during activated sludge treatment is possible by periodic restriction of aeration so that the microoganisms utilize nitrate as an oxidant(3) .

Chemical reduction is theoretically worthy of investigation as a process for practical removal of nitrate from domestic water supplies. The reduction techniques of the analytical chemists are impractical because a large excess of reagents and boiling water temperatures are used to force the reactions to completion. For a feasible process, complete removal is not required. In this laboratory, preliminary studies found that a smaller excess of reagents at reasonable temperatures gave reduction of nitrate in yields over 85 per cent(4). An extension of these findings seemed in order.

II. REVIEW OF LITERATURE

A method for reduction of nitrates during activated sludge treatment has recently been proposed by Ludzack and Ettinger(3) . The process is based on starving the organisms for oxygen at one stage of treatment so that the nitrate is used for oxidation. The nitrate is reduced to nitrogen gas and released to the atmosphere. Although this process is promising, it is applicable only to wastes that possess a food supply for microorganisms and not to stream water undergoing purification.

Chemical reduction of nitrate ion has been studied as a means for quantitative assay. Reduction of the nitrate to ammonia permits measure of the ammonia in distillates by titration.

Bremmer and Shaw(5) state that nitrate is commonly determined by reduction to ammonia using a mixture of iron and sulfuric acid, followed by distillation with alkali to release the ammonia. They describe a modification which substitutes as the reducing agent ferrous hydroxide precipitated with magnesium oxide. Quantitative reduction of nitrate occurs at room temperature after eighteen hours in a conway micro-diffusion unit or by boiling for thirty minutes.

Szabo and Bartha(6) discuss a nitrate assay using ferrous hydroxide with silver catalyst <u>at boiling temperature</u>. The reduction takes five to fifteen minutes and the amount of nitrate is measured by titrating the unoxidized ferrous ions with potassium permanganate.

Pepin-Lehalleur(7) used iron and sulfuric acid, <u>at boiling temperatures</u>, to reduce nitrate and observed a very low yield of ammonia, even though the reaction mixture showed no nitrogen at the finish. The use of excess iron and sulfuric acid gave no improvement in the ammonia yield.

An acceptable method for the examination of water or wastewater containing nitrate is based upon reduction with aluminum in strongly basic solution. The ammonia yield is substantially quantitative(8) .

Szabo and Bartha(9) postulate the mechanism of nitrate reduction by ferrous hydroxide as:

(1) $KNO_3 + 2Fe\,(OH)_2 + H_2O \rightarrow KNO_2 + 2Fe\,(OH)_3$

(2) $KNO_2 + 6Fe\,(OH)_2 + 5H_2O \rightarrow 6Fe\,(OH)_3 + NH_3 + KOH$

Step one takes place without catalysis while step two is slow and is catalysed by silver or copper. Metallic silver is present in a finely dispersed colloidal state whose stabilization is much enhanced by the alkaline medium. The catalytic effect is largly dependent on the particle size of the silver. The reaction is strongly pH dependent partly as a result of colloidal chemistry effects. The activity of the ferrous hydroxide is not permanent; the active centers are destroyed by excess of base and they become active again only at a very high pH. These authors feel that two kinds of reduction process occur simultaneously. In one case, active ferrous hydroxide reduces directly, and in the other mechanism the fine silver or copper sol takes the electrons from the less active ferrous hydroxide and transfers them to nitrate.

Brown(4) achieved excellent reduction of nitrate using excess ferrous hydroxide at high pH with copper catalyst near room temperature. The molar ratio used was approximately twice the theoretical ratio of eight to one (ferrous ion to nitrate ion). Under these conditions the nitrate reduction was 80 to 85 per cent in four hours with most of the nitrate being reduced to ammonia.

Summing up, biological nitrate reduction is possible but is not widely applicable. Rapid quantitative chemical reduction of nitrate ion has been reported only at boiling temperatures, but reduction adequate for a waste or water treatment process is possible in reasonable time intervals. The reported room temperature method requires a large molar ratio of reducing agent because of the valence changes of the respective ions.

III. OBJECTIVE OF INVESTIGATION

The objectives of the present investigations were to extend Brown's(4) findings concerning the reduction of nitrate with ferrous hydroxide and to explore other methods for chemical reduction. The parameters of interest were:

1. The minimum quantities of reagents required for adequate reduction.
2. The optimum pH for the reaction to proceed.
3. The cost comparison of alternate procedures, if any.

IV. METHODS AND MATERIALS

Reagents[a]

Acetic Acid, 99.7 per cent (Fisher). Used to adjust pH.

Boric Acid, (Fisher). Used to receive ammonia in the ammonia and nitrate assays.

Cupric Sulfate, $CuSO_4 \cdot 5H_2O$, (Baker). Used as a catylist.

Ferrous Sulfate, $FeSO_4 \cdot 7H_2O$, (Allied). Used as a reducing agent.

Iron Filings, 20 mesh (Baker). Used as a reducing agent.

Iron Powdered, Reduced by hydrogen, (Baker). Used as reducing agent.

Methyl Red, (Allied). Used as the indicator in the ammonia and nitrate assays.

Nitrogen, Bottled, (Industrial). Used to maintain anerobism.

Potassium Nitrate, (Allied). Used as the source of nitrate ion.

Sodium Hydroxide, Electrolytic Pellets, (Fisher). Used to adjust pH and to remove metal ions from solution.

Sodium Sulfite,(Fisher). Used as a reducing agent.

Sulfuric Acid, 95.0 per cent, (Fisher). Used to adjust pH and for back titration of ammonia in the ammonia and nitrate assays.

Zinc Dust, (Will). Used as a reducing agent.

Apparatus

Centrifuge, 50 ml, Model CL, (International).

pH Meter, Model N, (Beckman).

Mag-Mix Stirrer, Junior, (Fisher).

Con-Torque Stirrer, (Eberbach).

Shake Table, Model CS, (New Brunswick).

Kjeldahl Still, 6 unit, Wall Type, (Fisher).

Key to Manufactures

Allied: General Chemical Division, Allied Chemical and Dye Corporation, New York, N. Y.

Baker: J. T. Baker Chemical Company, Phillipsburg, N. J.

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a. Reagent grade chemicals used in all experiments.

Beckman: Beckman Instruments, Inc., South Pasadena, Calif.
Eberbach: Eberbach Corporation, Ann Arbor, Mich.
Fisher: Fisher Scientific Company, Fair Lawn, N. J.
Industrial: Industrial Gas and Supply Company, Bluefield, W. Va.
International: International Equipment Company, Boston, Mass.
New Brunswick: New Brunswick Scientific Company, New Brunswick, N. J.
Will: Will Corporation, Rochester, N. Y.

Analytical Methods

Two assays, ammonia and nitrate, are performed in this investigation. The assay procedure deviates sufficiently from the standard method(8) to justify a detailed description.

Ammonia Assay: To 40 ml of sample was added 10 ml of 2.5N sodium hydroxide, and centrifugation removed the reducing agent as the hydroxide. The supernatant was diluted with distilled water to 200 ml, of which 100 ml was distilled using 50 ml of boric acid solution (40 g./l.) to collect the condensate. Any ammonia present combined with the boric acid to form ammonium and borate ions, as follows(10) : $NH_3 + HBO_3 \rightarrow NH_4^+ + BO_3^-$. The ammonia was determined by back titration of the receiving solution with sulfuric acid to the methyl red end point. A suitable blank was used to correct for traces of ammonia in water and reagents.

Nitrate Assay: The 100 ml of solution not distilled in the Ammonia Assay was mixed with 5 ml of 2.5N sodium hydroxide (which raised the amount of base to 15 ml) and the mixture was added to a Nessler tube containing a strip of aluminum foil. The hydrogen evolved by the reaction of aluminum with sodium hydroxide bubbled through the solution and exited through a water trap to the atmosphere. This maintained a small positive pressure on the apparatus to insure that no atmospheric oxygen was admitted. The strongly reducing atmosphere of aluminum and evolved hydrogen reduces nitrate ion to ammonia. After a reduction period ranging from six hours to overnight, the ammonia (and thus the nitrate) was determined by the distillation technique already described.

In this laboratory, the nitrate assay, as presented, measured 90 to 94 per cent of the nitrate present in standards and was considered adequate for the proposed nitrate reduction studies.

Experimental Procedures

The principle lines of investigation on nitrate reduction were:

1. Reaction with ferrous hydroxide at alkaline conditions with copper catalysis.
2. Screening experiments with various reducing agents.
3. Follow-up on the screening experiments using a promising reaction with metallic iron at acid pH.

The detailed procedures used in the three test series were as follows:

Ferrous Sulfate Series

1. 720 mg. of potassium nitrate (100 mg. as N) in solution was added to samples of distilled water.
2. Various quantities of cupric sulfate in solution were added.
3. 23.7 g. of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in solution was added to provide 150 per cent of the ferrous ions needed for complete reduction.
4. The mixture was placed in a 1500 ml beaker and diluted to one liter with distilled water.
5. Nitrogen was continuously applied under the surface of the reacting mixture through a porous diffuser and the mixture was stirred magnetically.
6. The pH was monitored and continuously adjusted to a selected value with 2.5N sodium hydroxide.
7. Ammonia and nitrate concentrations were determined at elapsed times of ten minutes, one hour, and four hours.

Screening Series

1. 360 mg. of potassium nitrate (50 mg. as N) in solution was added to samples of distilled water.
2. The samples were diluted to 500 ml with distilled water and placed in 500 ml Erlenmeyer flasks.
3. Table 1 gives the reducing agent and catalyst concentrations used in each sample.
4. Each mixture was adjusted to a selected pH with 2N sulfuric acid or 2.5N sodium hydroxide. The exception being that one sample containing powdered iron and another containing powdered zinc, each with no cupric sulfate present, were adjusted to a low pH with acetic acid.
5. Each sample was capped and shaken twenty-four hours after which the pH was measured and the nitrate concentration determined.

Table I

Make-up for Screening Runs

Run	Reducing Agent	Concentration Reducing Agent	$CuSO_4 \cdot 5H_2O$
1 to 7	Powdered Iron	2.0 g./l.	none
8 to 14	Powdered Zinc	2.4 g./l.	none
15 to 18	Powdered Iron	2.0 g./l.	0.1 g./l.
19 to 24	Sodium Sulfite	4.0 g./l.	.002 g./l.

Metallic Iron Series

1. 720 mg. potassium nitrate (100 mg. as N) in solution was added to samples of distilled water.
2. Various quantities of powdered or coarse (20- mesh) iron were added.
3. The mixture was placed in a 1500 ml beaker and diluted to one liter with distilled water.
4. Nitrogen was continuously applied under the surface of the reacting mixture through a porous diffuser and the mixture was stirred mechanically in a vigorous fashion to keep the metallic iron suspended.
5. The pH was monitored and continuously adjusted to a selected value with 2N sulfuric acid.
6. Ammonia and nitrate concentrations were determined at selected time intervals up to six hours.

V. EXPERIMENTAL RESULTS

Ferrous Sulfate Series

The objective of this test series was to investigate the reduction of nitrate at room temperature by ferrous hydroxide as reported by Brown(4). Brown's findings indicated excellent nitrate reduction at pH levels greater than twelve using twice the amount of ferrous ion theoretically required. The present series used a 150 per cent overdose of ferrous ion and maintained constant pH in the mildly alkaline range. Also, the effect of different concentrations of cupric sulfate catalyst was evaluated.

Procedure. The procedure employed is stated in the Experimental Procedures section. Experiments one through seven were performed at various constant pH levels all with 1.0 g./l. $CuSO_4 \cdot 5H_2O$. Experiments eight through ten were performed at constant pH and varying total copper concentrations.

Results. The results are tabulated in Table 2. A preliminary ferrous sulfate-sodium hydroxide titration indicated that ferrous sulfate possesses buffering capacity at pH 8.0 and 10.3. In the course of the experiments it was noted that the pH kept continuously dropping and was difficult to maintain at pH levels lower than pH 10.3. It was also noted that the sodium hydroxide demand was greatest in the first three to ten minutes of the reaction.

Discussion. The results indicate nitrate reduction in all ten experiments. The trend is that the reduction proceeds more slowly and is less complete at the lower pH levels. This could be the result of greater solubility of ferrous hydroxide at decreased pH, or the catalytic properties of the copper sol may be affected adversly at the lower pH levels.

The greatest reduction of 90 per cent is seen to occur at pH 10.3 (Exper. 7). The buffering capacity at pH 10.3 was adequate to minimize the pH fluctuations. In the lower pH experiments the pH was difficult to control (including the pH 8.0 buffer range) and this could explain why the results of Experiments two, three, and four are not in better agreement.

Experiments eight, nine, and ten were performed at pH 10.3 to

Table 2

Nitrate Reduction with Ferrous Hydroxide[(a)] at Various pH Levels and Catalyst Concentrations

Exp.	(b) pH	$CuSO_4 \cdot 5H_2O$ (g./l.)	mg./l. as N						
			Initial	Ten Minutes		One Hour		Four Hours	
			NO_3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3
1	7.0	1.00	100	88	3	71	14	57	14
2	8.0	"	"	56	23	35	31	13	39
3	8.0	"	"	59	24	32	33	17	43
4	8.0	"	"	60	12	58	15	56	17
5	8.5	"	"			39	30	10	39
6	9.0	"	"	77	9	57	28	35	35
7	10.3	"	"	63	3	27	32	10	42
8	10.3	0.10	"	63	6	50	15	20	36
9	10.3	0.01	"	61	6	57	6	53	10
10	10.3	0	"	68	5	59	9	46	9

a. 23.7 g./l. $FeSO_4 \cdot 7H_2O$ was added to provide 150 per cent of ferrous ions required for complete reduction.

b. 2.5N-NaOH was used for pH adjustment.

evaluate the effect of cupric sulfate. The results indicate the catalyst had little effect in the initial reduction as indicated by the ten minute assay. However, increased reduction with increased catalyst occured after ten minutes. The experiments indicated that 80 per cent reduction takes place with 0.1 g./l. catalyst and that 90 per cent reduction takes place with 1.0 g./l. catalyst, both after four hours reaction time.

The fact that the ten minute nitrate assays fell in a narrow range indicates that the short term reaction is not dependent on the catalyst. It seems that the two mechanisms postulated by Szabo and Bartha(9) are independent. Initially, the surface of the ferrous hydroxide precipitate reduces directly <u>without catalytic aid</u>; and that adsorption, coagulation, or some other process changes the surface of the ferrous hydroxide particles rendering them less active. This phase takes place in ten minutes or less. Then the reaction proceeds at a slower rate with catalytic aid.

The discrepancy between the ammonia production and nitrate removal indicates that intermediate oxidation states of nitrogen are also produced. Except for nitrite ion, which is undesirable in itself and which may be reoxidized, the intermediate oxidation states are desirable because fewer ferrous ions would be needed to supply electrons than for transformation to ammonia.

In summary, 90 per cent nitrate reduction at pH 10.3 with ferrous hydroxide and cupric sulfate catalyst is possible. It may be feasible to eliminate the catalyst if active ferrous hydroxide can be maintained by formation of small quantities of fresh precipitate periodically.

Screening Series

Screening was performed to see if other reducing agents showed promise for nitrate removal. An arbitrary time of twenty-four hours was selected because a promising agent must show some reduction within this interval. A series of pH levels was studied for each system, but there was no attempt to monitor or control pH after the initial adjustment.

Procedure. The procedure used is presented in the Experimental Procedures section. The nitrate assay was modified in the case where sodium sulfite was used as the reducing agent by attempting removal of the reducing agent prior to distillation by aerating the sample for one hour.

<u>Results and Discussion</u>. The results are in Table 3.

Samples in which pH was adjusted with sulfuric acid or sodium hydroxide showed insignificant nitrate reduction. The pH in these samples drifted and in many cases went from acid to basic conditions or visa-versa. It was suspected that sodium sulfite would act as a nitrate reducing agent under any conditions but this was not the case.

The samples of interest are those with fine iron and fine zinc brought to a low pH with acetic acid. These samples remained acid over the twenty-four hour reaction time and excellent reduction was attained as shown by the 94 per cent reduction with iron and 85 per cent reduction with zinc. Evolved hydrogen was observed with the zinc but not with the iron.

It was decided that further investigation of iron under acid conditions would be undertaken.

Metallic Iron Series

The objective of this test series was to develop the most promising lead from the screening experiments.

<u>Procedure</u>. The procedure employed is stated in the Experimental Procedures section. Initial experiments were performed to find the optimum pH with 2 g./l. powdered iron present (vs. a maximum 1.59 g./l. theoretically required). Subsequent experiments were carried out at pH 2.5 to determine the amount of iron required for reduction and the effect of using coarse iron rather than powdered iron. One experiment was performed using primary settled sewage as dilution water, 2 g./l. powdered iron, and an iron nail (to check corrosion). The results of the sewage experiment were only fair and further work on this type of waste was deemed beyond the scope of this project.

<u>Results</u>. The results of the nitrate reduction experiments using 2 g./l. powdered iron at various pH levels are tabulated in Table 4. The calculations shown in Figure 1 indicate 94 per cent and 93 per cent nitrate reduction in five hours at pH 3.0 and 2.5 respectively.

The results of the five hour nitrate reduction experiments using various concentrations of iron at pH 2.5 are tabulated in Table 5. The data shown in Figure 2 indicate the following reduction of nitrate in

Table 3

24 Hour Nitrate Reduction with Various Reducing Agents and pH Levels

(a) Sample	Reducing Agent	pH Adjustment	Initial pH	Final pH	Nitrate Reduction (%)
1	Fine Fe (2 g./l.)	NaOH	11.0	10.4	13
2	"	NaOH	10.0	9.8	10
3	"	NaOH	8.0	8.9	15
4	"	H_2SO_4	6.0	9.0	18
5	"	H_2SO_4	4.0	9.0	16
6	"	H_2SO_4	3.0	7.9	17
7	"	Acetic Acid	3.0	5.2	94
8	Fine Zn (2.4 g./l.)	NaOH	11.0	12.0	14
9	"	NaOH	10.0	11.1	14
10	"	NaOH	8.0	10.2	12
11	"	H_2SO_4	6.0	10.1	17
12	"	H_2SO_4	4.0	10.0	12
13	"	H_2SO_4	3.0	6.3	13
14	"	Acetic Acid	3.5	4.3	85
15	Fine Fe (2 g./l.) $CuSO_4 \cdot 5H_2O$ (0.1 g./l.)	NaOH	11.0	11.0	10
16	"	NaOH	8.0	9.7	17
17	"	H_2SO_4	6.0	9.8	18
18	"	H_2SO_4	3.0	9.7	26
19	Na_2SO_3 (4 g./l.) $CuSO_4 \cdot 5H_2O$ (.002 g./l.)	NaOH	11.0	10.0	14
20	"	NaOH	10.0	9.3	12
21	"	NaOH	8.0	7.3	10
22	"	H_2SO_4	6.0	2.7	11
23	"	H_2SO_4	4.0	2.5	11
24	"	H_2SO_4	3.0	1.8	13

a. Nitrate concentration at start = 100 mg./l. as N

Table 4

Nitrate Reduction with Powdered Iron at Various pH Levels[(a)]

Time (hr.)	mg./l. as N			
	NO_3 at pH = 2.5	NO_3 at pH = 3.0	NO_3 at pH = 4.0	NO_3 at pH = 5.0
0	100	100	100	100
½		68	93	
1	25			85
1½		14	85	
2				
3	10	15	54	
4	11	8	49	84
5	7	6	40	81
6	5		39	79

a. 2 g./l. Powdered Iron; 2N-H_2SO_4used for pH adjustment

Table 5

Nitrate Reduction at pH 2.5[(a)] with Various Concentrations of Iron in Five Hours

Sample	Iron (g./l.)	mg./l. as N		
		Initial NO_3	Final NO_3	Final NH_3
1	1.06 (powdered)[(b)]	100	36	47
2	1.59 (powdered)[(c)]	100	14	66
3	2.00 (powdered)	100	7	
4	2.00 (coarse-20 mesh)	100	43	43

a. H_2SO_4 used for pH adjustment

b. Sufficient for: $Fe^o \rightarrow Fe^{+3}$ as $NO_3 \rightarrow NH_3$

c. Sufficient for: $Fe^o \rightarrow Fe^{+2}$ as $NO_3 \rightarrow NH_3$

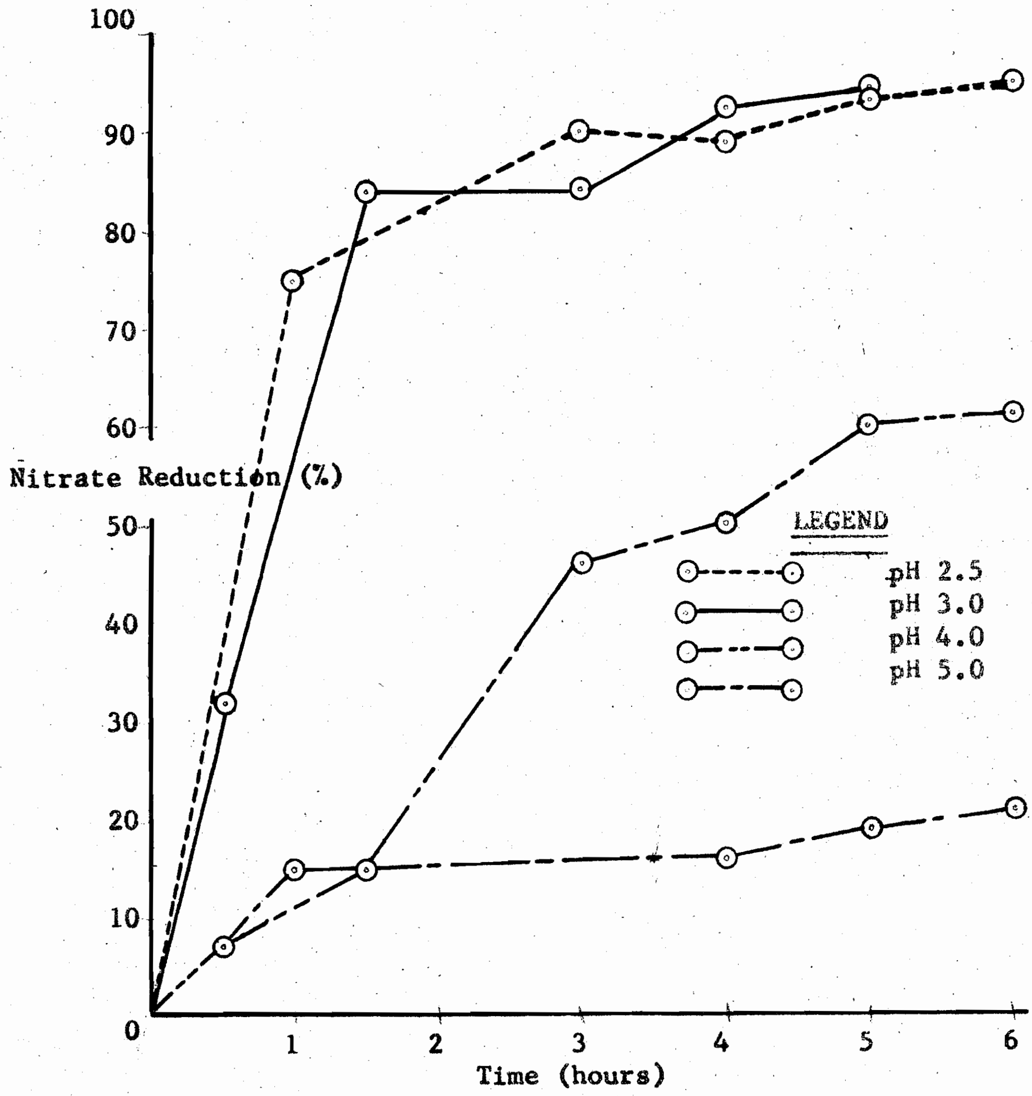

Figure 1. Nitrate Reduction vs Time at Various pH Levels with 2 g./l. Powdered Iron

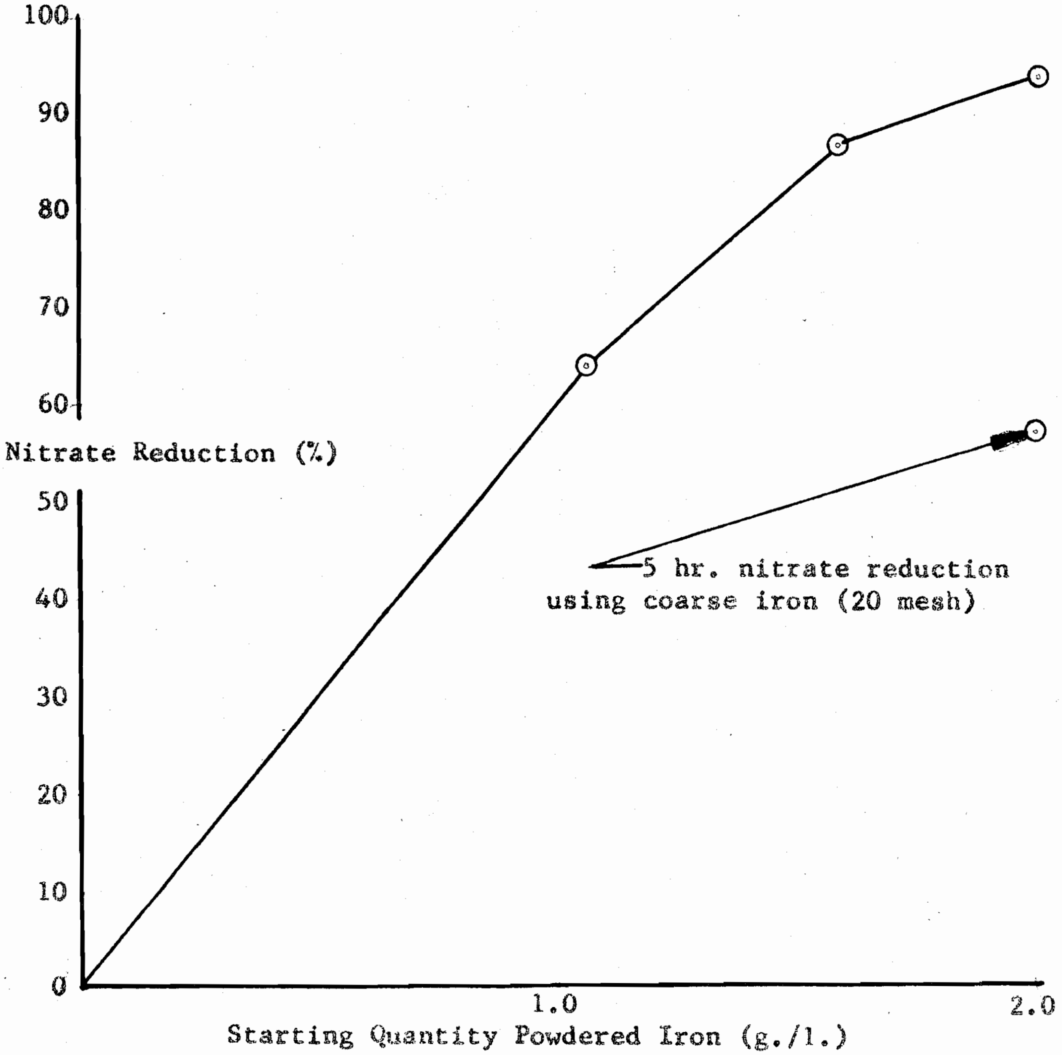

Figure 2. Nitrate Reduction vs Starting Quantity of Powdered Iron at pH 2.5 in 5 Hours

five hour reaction periods:

1. 1.06 g./l. powdered iron, sufficient for $Fe^o \rightarrow Fe^{+3}$ as $NO_3^- \rightarrow NH_3$, yielded 64 per cent reduction.
2. 1.59 g./l. powdered iron, sufficient for $Fe^o \rightarrow Fe^{+2}$ as $NO_3 \rightarrow NH_3$, yielded 86 per cent reduction.
3. 2.00 g./l. powdered iron, an excess, yielded 93 per cent reduction.
4. 2.00 g./l. coarse iron (20 - mesh), an excess, yielded 57 per cent reduction.

Nitrate reduction in the settled sewage was 25 per cent after five hours. The iron nail placed in the run with sewage showed no signs of developing a protective coating and a shining surface replaced tiny rust spots. At the end of this experiment it took 2.48 g./l. of lime ($Ca(OH)$) to neutralize the solution to pH 8 and precipitate the dissolved iron.

In all experiments, the iron removal step of the nitrate assay (neutralization with sodium hydroxide) resulted in a green precipitate.

Discussion. The results demonstrate that nitrate reduction using iron under acid conditions is quite promising. At pH levels of three or less excellent nitrate reduction occurs in five hours.

The principal oxidation-reduction mechanism seems to be: $Fe^o \rightarrow Fe^{+2}$ as $NO_3^- \rightarrow NH_3$. This is supported by the green ferrous hydroxide precipitate formed in the iron removal step of nitrate assay. Also, the theoretical quantity of iron for $Fe^o \rightarrow Fe^{+2}$ (1.59 g./l.) gives a nitrate reduction of 86 per cent whereas the iron for $Fe^o \rightarrow Fe^{+3}$ (1.06 g./l.) gives only 64 per cent reduction, both after five hours reaction. Ammonia is the principal end product in each case with 75 per cent of the nitrate reduced going to ammonia.

Coarse iron (20 - mesh) can be used for nitrate reduction although an excess is required. Two g./l. of coarse iron at pH 2.5 resulted in 57 per cent nitrate reduction in five hours. It is assumed that the excess is needed because of the decreased surface area with increased particle size. This is not a disadvantage because the excess required for rapid reduction could be added to a continuous process and could be supplemented as the iron dissolves. This is feasible because the surface of large iron particles does not become fouled as demonstrated by the iron nail in the settled sewage experiment.

The nitrate reduction in settled sewage was a disappointing 25 per cent after five hours using powdered iron at pH 2.5. Somehow, perhaps by competing oxidation-reduction systems, organic matter retarded the reduction.

To summarize, the results indicate rapid nitrate reduction using iron at pH 3 or less. The size of the iron particles is important as the rate of nitrate reduction is related to the surface area of the iron. Iron particles can probably be recovered and reused since their surface is not fouled. Nitrate reduction in sewage has been demonstrated but is incomplete and needs further investigation.

VI. DISCUSSION OF RESULTS

Of prime interest are the nitrate reduction reactions using ferrous hydroxide under basic conditions and metallic iron under acidic conditions. A nitrate reduction of 90 per cent at pH 10.3 with ferrous hydroxide and cupric sulfate catalyst was obtained, and slightly better than 90 per cent reduction was demonstrated using powdered iron at pH 3.

In the ferrous hydroxide experiments the molar ratio of ferrous ion to nitrate was twelve to one (the theoretical ratio is eight to one). This is a relatively large amount of iron and the voluminous ferric hydroxide precipitate may present a serious problem.

The manner in which the ferrous hydroxide experiments were performed necessitates the use of copper ion as catalyst. However, it was noted that during the first few minutes after the ferrous hydroxide was formed, the reduction proceeded without catalyst. This was assumed to be the result of the immediate activity of the ferrous hydroxide precipitate.

After the initial reduction, if the pH was less than 10.3, the pH was difficult to control. Also, the results of duplicate runs at pH 8.0 did not coincide. A possible explanation for the non-coincidence of the pH 8.0 runs may be sensitivity of the ferrous hydroxide crystal growth and activity to small differences in experimental conditions. At pH 10.3 a buffer zone overcame these difficulties. It is thought that by carefully controlling the formation of fresh ferrous hydroxide throughout the course of the reaction good reduction below pH 10.3 might be realized without catalyst.

A possible solution to the excessive sludge problem would be the reduction of ferric ion to ferrous ion, which would permit recycling the iron ions. Kuzminykh and Bomshtein(11) present the reaction kinetics involved in reducing ferric sulfate to ferrous sulfate with sulfur dioxide. Further research is required to find if this process can be applied to the rejuvenation of ferric hydroxide.

The pH difficulties present in the ferrous hydroxide reaction are absent in the metallic iron reaction because drift was slow and adjustment easy at all pH levels. Below pH 3 the reduction is excellent while at pH 3 to pH 5 the reaction is slower. Additional advantages of using iron is that iron offers two electrons to the oxidation-reduction reaction whereas ferrous ion offers only one and any undissolved iron would be reused. A disadvantage is the resultant dissolved iron which may constitute a disposal problem.

Thus in addition to extending Brown's(4) findings on ferrous hydroxide, this research has shown that metallic iron can be used for successful nitrate reduction. Further research on ferrous hydroxide could include: (1) Regeneation of ferric to ferrous ion. (2) Reduction of actual nitrate wastes. Further research on metallic iron could include: (1) Use of resultant ferrous ions for further reduction. (2) Reduction of actual nitrate wastes.

A minor disadvantage for both processes is the need for pH adjustment after the reaction. Also, both processes increase salinity.

The data indicate that further research may improve reduction with ferrous hydroxide at pH less than 10.3. Similarly, the iron has potential for development into a process to operate at pH levels above 3.0.

The comparison of raw material costs for the competing processes is presented in Table 6. The comparison was made by finding the amount and cost of the chemicals required for reduction, assuming ideal conditions, no excess of reducing agent, and complete reduction. The raw material cost of removing one mg./l. of nitrate as nitrogen from one million gallons of water would be Twenty-one Dollars for the ferrous sulfate method and Nine Dollars and Thirty-five Cents for the metallic iron method. Further economies will be possible if lime instead of caustic soda could be used or if ferric hydroxide could be regenerated to ferrous hydroxide.

To summarize, excellent nitrate reduction is possible using ferrous hydroxide or metallic iron. The metallic iron process is less complicated and less expensive. Further research may improve the cost and lessen the complications of the ferrous hydroxide method. Both processes suffer a disadvantage of requiring pH adjustment.

Table 6

Raw Materials Cost of Reducing Nitrate

Reducing Agent (a)	Ferrous Sulfate (b)	Iron (c)
lbs. Reducing Agent required to reduce one lb. NO_3 as N	86.6 lbs. @ $.0135/lb. (d) = $1.17	16.0 lbs. @ $.005/lb. (e) = $.08
lbs. NaOH required to reduce one lb. NO_3 as N	45.6 lbs. @ $.032/lb. (d) = $1.46	22.8 lbs. @ $.032/lb. (d) = $0.73
lbs. H_2SO_4 required on lb. NO_3 as N		31.7 lbs. @ $.0115/lb. (d) = $0.36
Cost of reducing one lb. NO_3 as N	$2.63	$1.17

(a) No excess of reducing agent used in computations.

(b) Equation: $NO_3^- + 6H_2O = 8Fe^{+2} \rightarrow Fe^{+3} + NH_3 + 9OH^-$

The NaOh quantity was computed from: $Fe^{+2} + OH^- \rightarrow Fe(OH)_2$

(c) Equation: $NO_3^- + 6H_2O + 4Fe^0 \rightarrow 4Fe^{+2} + NH_3 + 9OH^-$

The NaOH quantity was computed from: $Fe^{+2} + OH^- \rightarrow Fe(OH)_2$

(d) Price authority: Oil, Paint, and Drug Reporter, Vol. 182, No. 1, July 2, 1962.

(e) Price authority: Iron Age, Vol. 189, No. 1, June 28, 1962.

VII. CONCLUSIONS

This research has established parameters for the successful reduction of nitrate at room temperatures using two methods.

Nitrate reduction of 90 per cent can be achieved using ferrous hydroxide at basic pH or metallic iron at acid pH. Based on present knowledge of the reactions, the metallic iron method is deemed best from the engineering standpoints of ease of operation and cost. There is no reason to believe that this conclusion will change unless a ferric to ferrous reduction to compliment the ferrous hydroxide reaction is developed.

Future evaluation of the processes as applied to actual nitrate wastes is necessary.

VIII. SUMMARY

The U. S. Public Health Service drinking water standards specify an upper level of nitrate as 45 mg./l. (as nitrate). Consumption of waters containing a high level of nitrate ion causes "blue babies" and possible death of small infants.

Nitrate removal from water has been studied from the biological standpoint but this method is of limited application. A preliminary investigation by Brown showed that chemical reduction using ferrous hydroxide might be a practical removal method.

The objective of this thesis was to investigate the chemical reduction of nitrate using reducing agents in practical quantities at moderate conditions.

A number of reducing agents were studied under various conditions of pH. The research established the parameters for the successful reduction of nitrate at room temperatures using two methods. At pH 3 or less, using metallic iron as reducing agent, nitrate reduction was approximately 90 per cent complete. At pH 10.3, 90 per cent nitrate reduction occured using ferrous hydroxide as reducing agent and cupric sulfate as catalyst.

From the standpoint of ease of operation and cost, metallic iron seemed preferable. The raw material cost of reducing one mg./l. of nitrate as nitrogen in one million gallons of water was estimated to be Nine Dollars and Thirty-five Cents for metallic iron reduction.

Future research is needed to evaluate the processes as applied to actual nitrate wastes. Also, research on a ferric to ferrous reduction to regenerate the reagent for the high pH process would compliment this study.

IX. ACKNOWLEDGEMENTS

The author's entire graduate program was supported by a Public Health Traineeship Award from the Public Health Service, U. S. Department of Health, Education and Welfare.

The author expresses his appreciation to Dr. William A. Parsons for suggestion of the topic and helpful criticism; to his thesis advisor, Dr. H. R. Bungay for guidance during the research; and to his wife, Joyce, for her typing assistance and encouragement.

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XI. VITA

George Kenneth Young, Jr. was born in Pittsburgh, Pennsylvania, on September 11, 1939. After graduating from Boca Ciega High School, Gulfport, Florida, in June, 1956, he entered George Washington University in September, 1956. He transfered from George Washington University after one year of study, to Virginia Polytechnic Institute. While at Virginia Polytechnic Institute, the writer participated in the Cooperative Engineering Program and was empolyed at the Engineering Research and Development Laboratories, Fort Belvoir, Virginia, for three quarters; and at Fairfax County Department of Public Works, Fairfax, Virginia, for four quarters. He left Virginia Polytechnic Institute with a B. S. degree in Civil Engineering received in June, 1961, and returned in September, 1961, to pursue graduate study in Sanitary Engineering.

G. K. Young, Jr

Removal of Nitrates from Water by Chemical Reduction

Consumption of waters containing a high level of nitrate ion causes "blue babies" disease and possible death of small infants. The objective of this thesis was to investigate the chemical reduction of nitrate using reducing agents in practical quantities at moderate conditions.

Reducing agents were studied under various conditions of pH. The research revealed the parameters for the successful reduction of nitrate at room temperatures using two methods. At pH 3 or less, using metallic iron as reducing agent, nitrate reduction was approximately 90 per cent complete. At pH 10.3, 90 per cent nitrate reduction was achieved using ferrous hydroxide as reducing agent and cupric sulfate as catalyst.

The metallic iron reduction seemed best. The raw material cost of reducing one mg./l. of nitrate as nitrogen in one million gallons of water estimated to be Nine Dollars and Thirty-five Cents for metallic iron reduction.