

Iron and Manganese in Potable Water

by Clifford Caudy Young

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MASTER'S THESIS

C. C. YOUNG

CHEMISTRY THESIS.

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IRON AND MANGANESE IN POTABLE WATER.

The Determination of Manganese. The Occurance and Removal of Iron and Manganese.

In the presentation of this thesis the subject matter has been divided into three sections. The first to be a comparison of the different methods for the determination of Manganese in water with special reference to accuracy and availability for routine work.

The second to be devoted to the occurrence of Iron and Manganese in waters, the characteristics of such waters, and a survey of the State of Kansas to obtain some information as to the localities where such waters were to be found.

The third and last section to be a review of American and European practices and experience with Iron and Manganese waters, and the methods of removal when the waters are to be used as public supplies or for industrial purposes.

Comparison of Methods for Determination of Manganese.

The methods studied in connection with this work were:

1. Those in which the Manganese was precipitated as $MnO(OH)_2$
2. That in which the Manganese was precipitated as $MnCO_3$.

3. That in which the Manganese was precipitated as MnO_2 .

4. Those which depend on the precipitation of Manganese as MnS .

5. Those which depend upon the oxidation of all the Manganese to the permanganate condition.

In the cases of 1, 2 and 4, the iron must be completely separated from the Manganese before attempting precipitation. This can be done by removing the Iron as basic acetate then re-precipitating by ammonium hydroxide or by a double precipitation of the ammonium hydroxide.

1. In the methods where the Manganese is precipitated as $MnO(OH)_2$, the iron free solution containing Manganese is made slightly alkaline with ammonium hydroxide and the precipitation made with bromine, chlorine, hydrogen peroxide or hypochlorites. This precipitate can be treated in a number of ways. It can be heated and converted to Mn_3O_4 or dissolved in hydrochloric acid and precipitated as $MnNH_4PO_4$. This last has been worked over by Gibbs ^(R₁) and by Gooch and Austin ^(R₂), all of whom pronounce it very satisfactory. However, this method will not be available for determination of Manganese in water, for according to Hillebrand ^(R₃) and Treadwell ^(R₄) calcium and Manganese form manganites, which suffer precipitation with the basic oxide of Manganese

2. The precipitation of Manganese by means of ammonium carbonate ^(R₅) we can dismiss at once as not being

available for water, for calcium and magnesium would be precipitated at the same time.

3. The precipitation of Manganese as MnO_2 by means of nitric acid and potassium chlorate at boiling temperatures was first discovered by Beilstein (R6) and modified by Hampe (R7). This method is known as the Ford (R8) method in the United States. It was modified to make a volumetric end titration by Williams (R9) in 1882. This consisted of dissolving MnO_2 in standard ammonium ferrous sulphate and titrating back with potassium permanganate. The calculation was based upon the reaction $2 Fe SO_4 + MnO_2 + 2 H_2 SO_4 = MnSO_4 + Fe_2 (SO_4)_3 + 2 H_2O$. An attempt to apply this method to water was made by Prescher (R10), but he found that it was necessary to add 10% to the final results to have them at all accurate.

4. The precipitation of Manganese by means of ammonium sulfide is only applicable in the absence of nickel cobalt or zinc. To the filtrate from the iron is added 3 c.c. of ammonium hydroxide and hydrogen sulphide passed through the solution to the point of saturation, whereby Manganese is precipitated as sulphide. This is filtered off and weighed as $Mn_2 P_2O_7$, $Mn SO_4$ (R 11) or $Mn_2 O_3$. This method, according to Hillebrand (R12), is the best gravometric method for small amounts of manganese, but even in this case the error sometimes is very great and usually a plus one.

5. The principal methods which depend upon the oxidation of the Manganese to MnO_4 are:

cool, and when color has reached a maximum, either titrate with standard ammonium ferrous sulphate or make up to volume and compare with standard manganese sulphate solution as in Red Lead method.

The Bismuthate method (R18) was primarily used for determination of small amounts of manganese in steel. Blair (R19) states that he can successfully determine .0000005 grams of Manganese. The Manganese in nitric acid solution free from chlorides, is first treated with sodium bismuthate, boiled until the color of manganic acid has arisen to a maximum and then disappeared. By this means all organic matter is oxidized. The solution is then clarified, if any MnO_2 is precipitated, by adding $Na_2S_2O_3$. The clear solution is cooled and a second portion is added to bismuthate. After shaking and sedimentation, the liquid is filtered through a Gooch crucible and the color compared with the standard or titrated.

DETAILED METHODS OF PROCEEDURE.

Gravimetric Method By Means of Bromine.

A sufficient amount of water to yield 10 to 20 milligrams of Mn (usually 5 to 10 liters) is evaporated to dryness with HCl. Filter to remove SiO_2 . Precipitate the ~~Iron~~ ^{Iron} by means of NH_4OH filter and wash once or twice by decantation; dissolve the Iron in the same beaker in which original precipitation was made and re-precipitate with NH_4OH . Care should be taken to have plenty of ammonium salts present. The second precipitation is filtered and washed thoroughly. The two filtrates are evaporat-

ed to small volume (about 150 c.c.) and Bromine water added to the cold solution. The liquid is then boiled until the manganese is precipitated and the Bromine all removed. The basic oxide thus formed is filtered off, washed, dried, ignited in a porcelain crucible, and weighed as $Mn_3 O_4$. Gooch and Austin found (loc. cit.) ^{that} that this oxide varied considerably in composition, depending upon the conditions of ignition and as previously stated did not give good results when calcium and magnesium were present.

Gravimetric Method By Means Of Ammonium Sulphide.

The Manganese solution which has been freed from Iron as in the method just described is evaporated to approximately 200 c.c. To this is added 3 c.c. $NH_4 OH$, $H_2 S$ is then passed into the flask containing the solution to the point of saturation. The flask is tightly stoppered and set away for 24 hours or until the precipitation has settled. The precipitation of $Mn S$ is then filtered off through an S+S No. 589 filter. The precipitation is dried and the paper burned off in a porcelain crucible. A few drops of concentrated $H_2 SO_4$ are added to the crucible and evaporated to dryness. In conducting this evaporation, the crucible should be placed inside of a larger porcelain crucible and held in place by an asbestos ring. By this means an air space is maintained about the small crucible and the $H_2 SO_4$ will not spatter. After all $H_2 SO_4$ has been evaporated off both crucibles are placed on a triangle and heated to redness .. The precipitation is weighed as

Mn SO₄.

COLORMETRIC DETERMINATION OF MANGANESE BY AMMONIUM PERSULPHATE.

This method has the advantage over the one in which lead peroxide is used in that no filtration is necessary if the water has been freed from chlorids.

Methods.

Sufficient amount of water to give one to five milligrams of Manganese is evaporated with five cubic centimeters of concentrated sulphuric acid until fumes of SO₃ appear. Then the solution is heated until fumes are copiously evolved so that all hydrochloric acid may be driven off. The solution is then filtered to separate silica. To the filtrate is then added ten cubic centimeters of silver solution. If no turbidity is perceived, due to the precipitation of silver chloride, one gram of ammonium persulphate is added and the solution placed on the steam bath or hot plate. Very soon the pink color of permanganic acid begins to appear and rapidly increases to maximum. The flask may be removed after the color begins to show and placed in cold water when it has fully developed. The solution is then transferred to a Nessler jar and a comparison made with standards containing potassium permanganate of known strength.

Reagents.

Standard Permanganate solution. Dissolve .288 grams of potassium permanganate in water and make up one liter.

1 c.c. is equivalent to one-tenth milligram Manganese. The solution should be carefully standardized against iron. Silver nitrate solution containing two grams of the salt per liter.

Lead Peroxide Method.

The reaction employed in this method is that known as the Volhard Treadwell reaction.

Sufficient quantity of the water to yield one-tenth to one milligram of Manganese is evaporated with five cubic centimeters of sulphuric acid until copious fumes of SO_3 are given off. This should then be heated for some minutes to free entirely from chlorids. The solution is contained in a flask of about 150 cubic centimeters capacity, is then diluted with water to about 50 cubic centimeters. Twenty-five cubic centimeters of nitric acid (specific gravity 1.135) is then added. Sufficient red lead is then added so as to give a brown precipitate in the bottom of the flask. The mixture is then shaken and heated to boiling for two minutes. Allow precipitate to settle for a few moments and then filter through a Gooch crucible. The asbestos for the Gooch must be carefully prepared, washed and ignited so as to be free from organic matter. The filtrate is then made up to 100 cubic centimeters in a Nessler jar and compared with the standards made from known quantities of standard permanganate solution.

Reagents.

Standard potassium permanganate. Same as used in former method.

Red Lead powder, nitric acid (specific gravity 1.135)

This is made by using three parts water and one part of strong nitric acid (specific gravity 1.42).

Sodium Bismuthate Method.

Note. Evaporate with about 25 cc. of nitric acid (specific gravity 1.135) enough of the sample of water to give from 0.01 to 1mg. of Manganese. Gently ignite the residue or bake it for 1/2 hour at 130°. Add 50 cc. of nitric acid (specific gravity 1.135) and when the solution is cool add about 0.5 grams of sodium bismuthate. Heat until the pink color disappears.

At this point Blair, in his determination of manganese in iron adds sulphurous acid, ferrous sulphate or sodium thiosulphate, to clear the solution if manganese dioxide is precipitated, and heats it to dispell all oxides of nitrogen. With waters this step was usually unnecessary, but whenever so, thiosulphate was the reagent used.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 c.c. with dilute nitric acid.

In another tube put 100 c.c. of dilute sulphuric acid and add standard potassium permanganate solution until the color of the sample is matched. The volume of potassium

permanganate in cc. x 0.0001 gives the weight of manganese in grams. Express results as parts per million, -- milligrams per liter.

Reagents.

Potassium Permanganate Solution. -- Dissolve 0.288 grams of potassium permanganate in water and make up to 1 liter. 1 c.c. is equivalent 0.1 mg. Manganese.

Nitric Acid (specific gravity 1.135) A mixture of three parts of water and one part of strong nitric acid (specific gravity 1.42) is used.

Dilute Nitric Acid. 30 c.c. of strong nitric acid to the liter.

Sulphuric Acid. 25 c.c. of pure concentrated sulphuric acid to the liter. Add enough permanganate to color the solution slightly but perceptibly pink.

Asbestos. Prepare asbestos in the usual way by washing with acid and igniting. It should be free from organic matter.

NOTES AND PRECAUTIONS.

In case of waters containing considerable Chlorine such as the waters usually found in Kansas, it was necessary to evaporate the quantity of water taken to dryness with Sulphuric Acid and then take up the residue in nitric acid as above.

In removing the precipitate in the red lead method, also in sodium bismuthate method, advantage can be taken of the fact that the precipitates settle very readily. I have at times introduced the solutions containing these precipitates into a bottle and centrifuged for three

minutes. The supernatant liquid can then be poured into a Nessler jar and will be perfectly clear.

To test the accuracy and availability of the five methods a water was prepared by adding 1 liter of the standard permanganate solution to 8 liters of a water free from Mn. The KMnO_4 was reduced by means of SO_2 gas. One liter of this water contained 19. parts per million.

RESULTS OF ANALYSIS.
Parts per million.

	Bromine	Ammonium Sulphide	Pb O ₂	$\text{NH}_4)_2 \text{S}_2\text{O}_8$	Sodium Bis-muthate.
1.	23.37	17.13	19.03	19.03	19.00
2.	23.10	16.99	19.03	19.03	19.03
3.	23.10	17.12	19.03	19.37	19.03
4.	19.40	17.00	19.03	19.00	19.03

After working with these methods, the Author cannot draw other conclusions than those of Hillebrand (*loc. cit*) That with small amounts of manganese it is well to ~~disappear~~^{be used} with gravimetric methods and make use of one of the three colormetric methods. The degree of accuracy cannot be questioned and the time of making its determination is so short that they can be made a part of routine work without any inconvenience. In the survey of the Kansas waters which will appear in the next section, the Bismuthate method was used, on account of the high organic matter in many of its waters.

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PART II.

OCCURANCE OF MANGANESE AND IRON IN WATER, AND A SURVEY
OF THE WATERS OF KANSAS WITH REGARD TO IRON AND MANGANESE

The object of this survey was to acquire data from different parts of the State as to the amounts of Iron and Manganese that might be found when prospecting for new supplies.

The waters collected from five different sources as indicated in the following tables:

TABLE I.
Shallow Wells.

1.	Town	Solids	Parts per million	
			Iron	Manganese.
2.	Emporia	517.0	1.0	.304
3.	Mankato	706.0	3.0	none
4.	Lucas	612.0	1.1	none
5.	"	- - -	10.0	none
6.	"	- - -	3.0	none
7.	"	- - -	3.6	none
8.	"	- - -	4.0	none
9.	Smith Center	566.0	1.0	.44
10.	Downs	510.0	.5	none
11.	Beloit	508.0	none	none
12.	Oberlin	487.0	.3	.51
13.	Seneca	378.0	.1	none
14.	Plainville	320.0	none	none
15.	Logan	- - -	.1	.12
16.	Greenleaf	491.0	.7	none
17.	Ellsworth	992.0	.5	.35
18.	Norton	462.0	3.0	1.51
19.	Stockton	709.0	2.0	.59
20.	Havensville	1039.0	.4	.45
21.	Florence	872.0	.5	none
22.	Hays	469.0	1.0	none
23.	Hays			.55
24.	Peabody	830.0	.5	trace
25.	Caldwell	458.0	2.0	trace
26.	Lyons	456.0	.1	trace
27.	Osborne	377.0	.3	none
28.	Herington	608.0	.1	trace
29.	Sterling	- - -	.1	.036
30.	Waverly	546.0	.2	none
31.	Clifton	350.0	.2	none
32.	Lindsborg	723.0	.7	.28

Town	Shallow Wells.		Parts per million.	
	Solids	Iron	Manganese	
33. Wilson	575.0	.7	trace	
34. Wilson	293.0	1.7	trace	
35. Arkansas City				
well	1295.0	4.0	.942	
36. " " tap	830.0	.3	.196	
37. " " well	1577.0	1.5	none	
38. Moundridge	392.0	.1	none	
39. Hanover	1239.0	1.5	trace	
40. Lebanon	555.0	.5	none	
41. Holton	454.0	1.0	none	
42. Wichita	1154.0	.4	none	
43. " "	462.0	.3	none	
44. Lincoln	632.0	.9	none	
45. Eldorado	418.0	trace	trace	
46. Claycenter	994.0	trace	.16	
47. Hiawatha	407.0	trace	.32	
48. Harper	294.0	none	none	
49. Concordia	587.0	.15	.47	
50. Argentine	956.0	8.0	1.35	
51. Manhattan	487.0	.7	.54	
52. Wellington	988.0	.2	none	
53. Junction City	375.0	.3	none	
54. Bonner Springs			.52	
55. St Marys			trace	
56. Wamego			trace	
57. Topeka			.74	
58. Wakefield			.26	
59. Lawrence	495.0	10.36	2.60	main well
60. " "		3.5	1.34	tap water
61. " "			1.12	"
62. " "			1.30	"
63. " "			1.19	"
64. " "			.74	"
65. " "			1.15	"
66. " "			1.30	"

TABLE II.

Deep Wells.

Town	Solids	Parts per million.		
		Iron	Manganese	H ₂ S
1. Mineral	978.0	10.0	none	present
2. Sedan	412.0	.1	none	present
3. Chetopa	859.0	none	trace	
4. Ellinwood	761.0	none	trace	
5. Frankfort	456.0	.3	trace	
6. Halstead	283.0	.3	.12	
7. Liberal	345.0	1.0	trace	
8. Stafford	377.0	.1	none	
9. Goodland	287.0	.1	none	
10. Wilson	358.0	.3	none	
11. Alma	457.0	1.5	.12	
12. Sabetha	399.0	.5	none	
13. Great Bend	562.0	.1	none	

3.
Deep Wells.

Town	Solids	Parts per million.		
		Iron	Manganese	H ₂ S
14. MaPherson	421.0	.3	.129	
15. Frontenac	496.0	.3	trace	
16. Belleville	808.0	.7	.288	
17. Columbus	496.0	.3	.200	
18. Pittsburg	518.0	.5	none	
19. Hutchinson	785.0	.1	.078	
20. Dodge City	491.0	.3	trace	
21. Weir City	521.0	.3	none	present
22. Newton	253.0	.15	none	&

TABLE III.
Springs.

Town	Solids	Parts per million	
		Iron	Manganese
1. Cottonwood Falls	348.0	.3	none
2. Kingman	196.0	1.5	none
3. Wilson	295.0	.2	none
4. Arkansas City	377.0	.1	none
5. Conway Springs	144.0	.1	none
6. Abilene	332.0	.1	trace

TABLE IV .

Town	Rivers. Solids	Parts per million	
		Iron	Manganese
1. Galena	164.0	none	trace
2. Arkansas City	440.0	.5	.078
3. " "	1546.0	5.0	.824
4. Medicine Lodge	241.0	3.0	trace
5. Osawatomie	403.0	.6	trace
6. La Harpe	335.0	1.5	trace
7. Gas	255.0	.5	none
8. Wichita	506.0	.5	.078
9. Coffeyville	493.0	3.5	.628
10. Paola	274.0	.5	none
11. Council Grove	406.0	.3	none
12. Burlington	539.0	.5	.0785
13. Humboldt	513.0	.3	trace
14. Parsons	232.0	1.0	trace
15. Fort Scott	257.0	.5	.117
16. Atchison	659.0	7.0	.157
17. Oswego	465.0	.3	.196
18. Fredonia	380.0	.7	.196
19. Winfield	394.0	1.0	.196
20. Independence	334.0	3.5	trace
21. Emporia	473.0	6.5	.304
22. Iora	471.0	.3	.078
23. Chanute	333.0	.2	.078
24. Ottawa	423.0	2.5	.235

TABLE V.

Town	Artificial Lakes.		
	Parts per million.		
	Total solids	Iron	Manganese
1. Osage City	443.0	1.0	.3928
2. Horton	342.0	2.0	.258
3. Cherryvale	129.0	2.5	none
4. Olathe	208.0	0.7	.12
5. Baldwin	100.0	5.0	.377
6. " Filtered	108.0	-. -	.17
7. Pleasanton "	200.0	3.9	.111
8. " " unfiltered.	230.0	30.2	1.86

CHARACTERISTICS OF TYPICAL IRON-CONTAINING WATERS.

Theoretical. ⑥

When typical ground-waters containing Iron are freshly drawn, they are clear and colorless or nearly so, contain high amounts of carbon dioxide, sometimes considerable methane or hydrogen sulphide, and are deficient in oxygen. They have the styptic or "inky" taste which is characteristic of Iron. When sufficient oxygen has had access to the water, it becomes turbid with oxidized insoluble iron, which after a shorter or longer time gathers into flocs and finally precipitates, leaving the water itself colorless and free from Iron. Where there is no purification plant, this precipitation takes place in the distribution system; tea made with the water is black; rust spots appear on linen, and white plumbing fixtures are stained with iron rust. After a

⑥ Robert Spurr Weston. Transactions of American Society C. E. Sept. 1909. page 117.

sudden disturbance, as after a large fire, the water is exceedingly turbid with precipitated iron oxide. In some cases a fungus, *Crenothrix*¹, grows in the pipes, feeding upon the organic matter and causing a precipitation of the iron contained in the water. Frequently the growth of this organism chokes service pipes and small mains, while the odors due to its death and decomposition become extremely disagreeable.

Manganese-containing waters have similar characteristics, except that the precipitation is slower and the stains and deposits are much darker in color. Certain ground-waters contain a little alumina, which behaves in much the same way, but, because the precipitate is white, it has never been known to cause trouble, although it is known to accompany the growth of *crenothrix ochracea*².

Character of Ground-Water.

Like other natural products, ground-water containing Iron and Manganese varies greatly in its composition, as shown in Tables 1 to 5.

The primary sources of Iron in ground-water are the ~~xxx~~ deposits of Iron in the earth's crust, amounting, according to Mr. F. W. Clark³, to 5.46%, that is, the fourth in importance of the elements composing the earth. The solvent of the Iron is the ground-water itself, aided by the acids dissolved in it. It has been stated by many writers,

and it is quite commonly believed, that Iron exists in water as a salt of one or more of the acids, chiefly as ferrous carbonate; but Whitney⁴ has proved that absolutely pure water, free from oxygen and carbonic acid, will dissolve an appreciable amount of metallic iron. The force which causes this solution (the "solution pressure") is an electrical one. Iron has a natural tendency to go into solution. It is a well known fact that if a piece of bright iron be immersed in a solution of copper sulphate, the metallic copper will be plated out on the iron, and the iron will replace the copper in the solution as shown by the following equation:

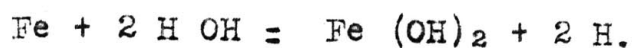


The explanation of this phenomenon, according to the modern theory of solutions, is that copper sulphate is an electrolyte⁵ and in a solution is partially dissociated into its ions, Cu and SO₄. There are present in the solution the positively charged copper ions which have less solution pressure than the positively charged iron ions; hence the former are attracted to the negatively charged metallic iron; the electric charges are neutralized, and the metallic copper is precipitated. This action continues because the copper is a conductor and does not re-dissolve in the presence of Iron for the reason explained above.

Water, like copper sulphate, is dissociated to a small degree into hydrogen, H +, and hydroxyl, OH-. Its formula may be written as



From an electro-physical standpoint, hydrogen is a metal and acts like copper; that is, it plates out on the metallic iron at the negative pole, while the iron takes its place in solution. However, the hydrogen is not liberated readily upon the surface of the iron, and soon the condensation of gaseous hydrogen which is a non-conductor, on the surface of the iron checks the action. In order that the solution of iron may proceed further, the force which prevents the hydrogen from being liberated as a gas on the surface of the Iron must be overcome. This is accomplished by what the physical chemists term over-voltage; that is, it is necessary to increase the concentration of the hydrogen ions in the solution in order to force the liberation of hydrogen gas, or, as one may say, that the bubbles of gas may be crowded off the surface of the Iron. Then the Iron goes into solution as ferrous hydrate, hydrogen being evolved. The equation is as follows:



Acids like carbonic acid (H₂ CO₃), or sulphuric acid (H₂ SO₄), added to water greatly increase the concentration of the hydrogen ions and promote solution; while alkalis like lime Ca(OH)₂ or caustic soda Na

OH, increase the concentration of the hydroxyl ions and check solution.

Dr. Ahlerton S. Cushman,⁵ Professor W. H. Walker, and others⁶ have shown that a piece of ordinary iron which is never homogeneous, immersed in water acts like an electrolytic couple, that is, it produces electric currents, the particles of metallic iron acting as positive poles, and the particles of carbon, graphite or scale, as negative poles. They have shown that the hydrogen is deposited and later given off at the negative poles, while the solution of iron in the form of ferrous hydrate takes place at the other. In an acid water, the one which corrodes iron most readily is that which has the largest excess of hydrogen ions.

The conclusion from all these studies is that, in the absence of oxygen, iron exists in water as the ferrous or oxidized hydrate. This is quite soluble in water; in the amounts usually found in water, entirely soluble.

The Iron in water may be from vegetable or mineral sources. The mineral sources are the iron silicates, carbonates, sulphates, chlorides, phosphates, oxides, etc. The chief vegetable source is the iron in plants, living and dead, beginning with the green chlorophyll of the leaves of plants, a compound of Iron, and extending through leaf mould, peat, and lignite, to

anthracite. Generally speaking, all these compounds are derivatives of oxides.

These deposits of iron are more or less soluble in water which is free from oxygen, and especially so in water containing acid. The degree of solution is proportional to the amount of the acid, because it is the excess of hydrogen ions which effects solution: Carbonic acid is most important in this connection, not because it is a strong acid, which it is not, but because its amount is usually far greater than that of any other acid present in water.

The primary source of carbonic acid is the organic matter in the soil. The rain water which falls on the earth is saturated with oxygen, and, before its passage through the ground, it will not dissolve Iron from mineral although it may from vegetable sources. The upper soil layers are rich in organic matter; the organic matter under goes oxidation, oxygen is absorbed and carbon dioxide is evolved - the water loses its oxygen and becomes charged with carbonic acid. More extended decomposition of organic matter in the absence of oxygen may produce hydrogen sulphide and methane. One or both of these gases may be dissolved in ground-water, according to its previous history, and increase its solvent power. The occurrence of a black peaty layer overlying white sand containing iron, the white sand in turn overlying red sand containing

oxidized iron, is a familiar sight to all engineers who have made excavations. Here the carbon dioxide produced by the decomposition of the organic matter has caused the solution of the iron from the upper layer, has carried it down through the white sand, and has kept it in solution until the iron has become oxidized and reprecipitated in the layer beneath. Wells sunk beneath such soil may be free from iron at first, but continued pumping may cause so much water to pass through the soil that it is robbed of its small amount of oxygen when the iron goes into solution and appears in the well water. This case is met frequently in practice.

It is stated by many geologists that carbon dioxide is frequently of volcanic origin, resulting from the decomposition of iron oxide at high temperatures. This may explain the presence of iron in the waters of deep wells far removed from any deposits of organic matter. The organic acids for example, carbonic and apocrenic acids, may also aid the solution of iron. The waters of certain Brazilian rivers which contain large amounts of organic acids are said to be very corrosive, and the bottoms of iron boats are attacked rapidly. The production of hydrogen sulphide in the presence of iron and organic matter results in the formation of ferrous sulphide. This is insoluble, but if exposed to the air it readily oxidizes to ferrous sulphate which is very

soluble in water. This usually the explanation of the presence of ferrous sulphate in the so-called "acid iron" waters.

As stated later, Manganese sulphide behaves in a similar manner, with the formation of manganese sulphate and, in the absence of alkalies, of free sulphuric acid, which in turn effects a rapid solution of the Iron and Manganese with which the water comes in contact.

Iron (or Manganese) in water may be: (1) In the unoxidized or ferrous condition, when it is soluble in water; (2) In the oxidized or ferric condition, when it is almost insoluble in water containing oxygen; (3) In the colloidal or semi-soluble form, when it may be oxidized, yet to all outward appearances in solution. Perhaps there is, in addition, an insoluble, vegetable compound of iron which is present in the colloidal form.

According to Schwere^s such a vegetable compound of iron is produced by the oxidation of organic matter to organic acid by ferric hydrate. The organic acid thus formed combines with the iron to form an insoluble organic salt of iron which is exceedingly difficult to treat. This compound is formed after the water is drawn from the ground and after a portion of the iron has oxidized.

Ferruginous ground-waters are of three general classes: (1) Those which begin to precipitate the

Iron immediately after aeration, like many of the waters of North Germany; (2) Those which will hold the iron in solution indefinitely, even after aeration like the dark brown water of deep wells or the acid waters from mines; (3) Those which precipitate a part of the iron within a few hours and hold the remainder in solution indefinitely, like the water at Reading, Mass.

Clear and colorless ferruginous ground-waters never contain oxygen. When both oxygen and iron are present, the water is either turbid or colored. In the latter case the iron is held in solution or suspension by vegetable matter.

The amount of iron in water varies from a slight trace to more than 2,500 parts per million. Manganese does not usually occur in large amounts, although on one occasion more than 220 parts per million were found in the Breslay supply. As a rule however, the waters used for water supplies contain less than 10 parts of Iron per million and only small amounts of Manganese. The average Iron content of certain ground-waters is given in Table 6, which also indicates roughly the geographical distribution of ferruginous water. It will be deduced that the ground-waters of Bavaria, Baden, Austria, Switzerland, Scandinavia, Italy, and parts of North America, seldom contain Iron, and it is believed that the same is true of large parts of Russia, Siberia, Asia Minor,

France, and the Spanish Peninsula, although analytical data are wanting in this connection. The writer has not been able to obtain very much information, concerning the Iron content of the waters of the British Isles. It is a well-known fact, however, that some of the hard well waters of England contain more or less Iron, and that it can be removed by the softening process.

Generally the waters which contain Manganese contain still more Iron. In one case, however, at

TABLE 6.
Amounts of Iron in Various Ground-Waters.
(Parts per million of Iron)

Locality	Iron
Aguas de Var, Spain	61
Arad, Hungary	25
Asbury Park, N. J.	9.1
Aurich (Friesland)	19.2
Berlin, Muggelsee	1.3
Berlin, Tegel	1.0
Blanchimont, Belgium	21.3
Bloomfield, Conn.	15.
Brunswick, Germany	6.0
Bree, Belgium	6.8
Breslau, Germany	6 to 400
Centreville, Iowa	3.2
Charlottenburg, Germany	1.4
Chaddfontaine, Belgium	6.3
Chevron, Belgium	40.6
Cohasset, Mass	1.3
Court St. Etienne, Belgium	6.3
Diepenbeck, Belgium	4.
Far Rockaway, N. Y.	2.48
Garrettsville, Ohio ⁹	2.0
Glogau, Germany	5.8
Haile, Germany	0.8
Hamburg, Germany	2.0
Hanover, Germany	0.5
Huy, Belgium	8?
Indianapolis, Ind.	41.
Joplin, Mo.	0.3

State Board of Health has made a study of the 78 ground-water supplies in the State in use at the end of 1905¹⁴. One of these supplies Bradford, was so bad that it was abandoned; the supply at Reading has to be purified; that at Marblehead is to be purified, and many of the others now contain objectionable amounts of Iron which should be removed. Table 8, abstracted from the report, shows how the amounts of Iron have increased in ten years. No results of tests for Manganese have been published.

Figure 3, shows the increase in the amount of Iron in the Reading water supply.

TABLE 8. water
The Amounts of Iron in Certain Massachusetts Ground-Waters.

City or Town	To 1895	1896-1900	1901-1905
Amesbury.		0.40	0.67
Billerica		0.18	0.36
Brookline	0.02	0.03	0.15
Fairhaven LL	0.01	0.12	0.15
Farmingham	0.14	0.10	0.14
Hyde Park wells (near Neponset River) . . .	0.14	0.16	0.41
Lowell, Boulevard wells. .		0.32	0.32
Marblehead	0.38	1.19	2.03
Methuen	0.13	0.09	0.28
Middleboro.	0.19	0.35	0.96
Newton	0.12	0.06	0.13
Waltham	0.04	0.15	0.31
Wellesley		0.05	0.08
Winchendon.		0.09	0.28
Woburn	0.01	0.02	0.05

The Board reports that:

" The deterioration is usually most marked in those sources which are located near a pond or stream

the water being derived in such cases in part from the rain which falls upon and sinks into the ground in the neighborhood of the collecting works, and in part by percolation through the ground from the neighboring surface source. ----- ".

"Iron is frequently present in water which has passed through peat and other soil containing a large quantity of organic matter and which has not ~~be~~ been subsequently purified in its passage through sand or gravel to the collecting works; and in some cases the deterioration of ground-waters has been due to the reduction in efficiency of the filtration of water which has taken up organic matter and iron ~~fr~~ from peat or much near the surface of the ground. An example of such deterioration is found in Billerica where the wells are located in the midst of an ex-meadow which contains at the surface a deep deposit of organic matter ".

The Board also demonstrates that increased draft is often responsible for the deterioration in the character of the water. " At Lowell a great improvement was made in the quality of the water drawn from the ground in the vicinity of the Merrimack River by an extension of the collecting works." A like improvement has been observed in other places, but it is usually of a temporary character only.

There has been an unfortunate tendency in cases where the Iron has increased, as in the above,

to abandon the ground-water supply, with its invested capital, and seek another source. Such a ground-water purified, would be safer than a filtered surface-water, and in most cases more economical. "

OBSERVATIONS AND CONCLUSIONS.

During the progression of the survey of Kansas waters for Iron and Manganese, several notable instances of secondary concentration of Manganese were found. There are some very interesting deposits of MnO_2 in Meade County, which consist of pure quartz sand covered with a coating of MnO_2 so that the grains at first sight might easily be mistaken for magnetic ^{tite} sand.

Many similiar deposits have been noted in Western Kansas by Professor Haworth. This fact lead to the examination of surface waters Table 4 & 5 and is ample explanation for the large number of surface waters containing Manganese.

The part organic matter plays in the solution of Manganese and Iron has been discussed at the beginning of this section, however, one point was not brought out. Waters containing Iron and Manganese often come to the laboratory which yield unnatural amounts of free ammonia and the evidence indicates so pointedly that there is some between Iron and Manganese and the high free ammonia. The author feels that some mention should be made of the theories relating to this subject. example:

Table 9.

	Belleville	Osage.
	Parts per Million.	
Turbidity	50	140
Color	Iron rust	Iron rust.
N _o s NO ₂	.0005	none
" NO ₃	none	trace
" FneNtl ₃	.28	1.34
" Alb NH ₃	.096	.244
Cl	48.	80.
HCO ₃	478.7	838.4
Solids	734.	5810.
Fe	20.	54.

Klutt¹⁵ accounts for the high free ammonia in water contain Manganese and Iron by saying that ammonia in deep waters containing Iron comes from two sources, namely the action of bacteria and the chemical action. In the latter the nitrates and nitrites together with carbondioxide from the surface, in passing downward come in contact with (Fe S₂ and Mn S). A change occurs in which the Iron and Manganese are converted to the bicarbonates with the liberation of H₂S which reduces the nitrates and nitrites to NH₃. He substantiates these statements with laboratory experiments in which he claims to have obtained NH₃ from the action of carbon dioxide on iron sulfide and subsequent reduction of the nitrates.

H. Noll¹⁶ repeated the experiments with negative results and Klutt explains the difference in results by the fact that they worked with different samples of the metallic sulphides. Although Klutt's theory may not offer the correct explanation of the phenomenon of high free ammonia in the presence of large amounts of Iron his experiments will bear working over, although Noll questions his results.

CONCLUSIONS.

A comparison of the tables of analysis of Kansas waters with a map of the state leads to the conclusion that the greatest care must be ^{exercised} any place in the state to avoid secondary deposits of Iron and Manganese that are likely to cause trouble in water supplies.

The geological formations of the country are so miscellaneous in character that at any point in the alluvial formation Iron and Manganese are liable to contaminate a supply taken from shallow wells in river bottoms. Springs are less likely to contain Manganese and Iron for they come largely from the limestone formation. Surface waters all contain some Manganese depending to a large extent upon the time of year, rain-fall and run-off conditions just previous to the time of taking the sample .

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PART 111.

THE REMOVAL OF IRON AND MANGANESE FROM WATER SUPPLIES.

REMOVAL OF IRON AND MANGANESE.

The problem which confronts a city whose water contains large amounts of Iron and Manganese is very troublesome, and instead of putting into operation some efficient method of removal many public supplies have been abandoned.

The principles upon which most Iron removal plants depend are: First: The Iron and Manganese must be oxidized. This is accomplished by aeration. Second, the oxidized Iron and Manganese must be changed from the colloidal condition to the precipitated hydroxides. Many factors influence this change and have all been made use of in the design operation of Iron removal plants. They are as follows:

Presence of electrolytes.

Presence of alkalies.

Agitation and friction.

Temperature, pressure and concentration.

Contact with filtering material or $\text{Fe}(\text{OH})_2$.

Presence of Humus Compounds.

Mr. Robert Spurr Weston, in a paper read before the American Soc. of Civil Eng. (Proceedings of the Soc. Sept. 1909) has given a complete history of the development of all Iron Removal plants both in Europe

and America. This very excellent paper gives a summary of all the important engineering work along this line that had been done up to the time the paper was printed. Mr. Weston tabulates the "Development of the Iron removal plant" as follows:

TABLE 12.
Development of the Deferrization Processes.

Process.	Inventor and system	Date of introduction.
Aeration followed by filtration through fine gravel or coarse sand.	(Salbach (Gravel aerator)	1868
	(Anklam (Cascade aerator)	1880
	(Oesten (Spray aerator)	1890
	(Piefke and Proskauer (Coke sa aerator)	1891
	(Wellman (Brick-filled aerator)	1894
	(Beer and Thiem (Wooden-slat aerator)	1902
Filtration without aeration by pressure filters	(American pressure filters (Sand and bone charcoal)	1894
	(von der Linde and Hess (Tin oxide-impregnated shavings . . .	1897
	(Helm (Danzig) Magnetic iron ore	1902
	(Bock (Hanover) (Plain shaving)	1903
Treatment with metallic iron and filtration.	(Clark (Filtration through fine coke or iron chips	1895
	(Town of Reading (Electrolytic iron)	1904
Intermittent filtration through coarse sand	(Dunbar and Kryck	
	(
Chemical treatment and rapid filtration.	(Krohnke (Lime without aeration)	1891
	(Cumberland Mfg. Co. (Reading) (Lime and sulphate of alumina with aeration)	1894
	(Weston (Clay and sulphate of Alumina	1906
	(Gans (Filtration through cal- cium aluminum silicate.	1907
	(Schwerts (Ferric chloride, slow filters	1907

TABLE 12 (cont)

Process.	Inventor and system.	Date of in- troduction.
Precipitation by mixture of iron - containing water with colored deep- well water, follow- ed by rapid fil- tration.	Wernike and Mertens (Posen)	1905.

Mr. Weston concludes from his extensive investigation that the knowledge of removal of Iron and Manganese has been extended in the last few years to a point where the Iron and Manganese can be removed in most cases from a water supply of any consequence cheaper and with less difficulty than would be experienced in locating and developing a new supply.

April 21, 1911.

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