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IRON REMOVAL USING MAGNESIUM OXIDE

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HISTORY OF CALCINED MAGNESITE PROCESS

In 1961, the Massachusetts Health Research Institute, in cooperation with the Massachusetts Department of Public Health and other agencies, conducted studies at Amesburg, Lowell and Billerica, Mass., on the removal of iron and manganese from ground waters using diatomaceous earth filtration (4). A significant result of these studies was the observation that near-complete iron removal could be obtained by aeration, the addition of small quantities of magnesium oxide during a short period of rapid mixing, and diatomaceous earth filtration.

More detailed studies on the use of magnesium oxide for the precipitation of iron were reported by Bell (2) in 1965. A pilot water treatment plant consisting of an aerator, stirred reaction tank and diatomaceous earth pilot plant was used to filter Billerica and Lowell, Mass., well water. Near-complete iron removals were obtained by the addition of from 5 mg per l to 20 mg per l of MgO and by providing 5 min to 10 min of rapid mix. The addition of strong oxidants, such as KMnO_4 , resulted in the formation of a ferric iron precipitate which resulted in short filter runs. The addition of MgO, on the other hand, resulted in prolonged filter runs without a visible precipitate being observed. Bell speculated that the surface solubility of the MgO particles might be responsible for the observed rapid ferrous iron removal over a pH range of at least five to nine. Subsequently, Bell (3), a study of manganese removal, suggested a two-step process for the removal of iron and manganese. Iron would first be removed by the addition of MgO to a stirred reactor and manganese would be oxidized by KMnO_4 thereafter. This would result in reduced chemical costs.

In 1968, Wolfner (8) reported on the design and construction of an iron

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removal plant employing MgO at Point Pleasant Beach, New Jersey. The plant is a compact installation capable of filtering up to 1.25 mgd. The cost of the plant including a high-lift 5-mgd pumping station was just under \$200,000 while the chemical costs have been observed to be about \$10 per million gal treated.

This sequence of studies and events has indicated that the calcined magnesite-diatomaceous earth process is competitive for iron removal. Although a substantial amount of empirical data has shown that the process has wide applicability to waters throughout the United States, no information has yet been obtained from controlled laboratory studies which describe the mechanism of the reaction or the kinetics of the iron removal.

DESCRIPTION OF PROCESS

The calcined magnesite-diatomaceous earth filtration process for iron removal includes the addition of light-burned, chemical grade magnesite

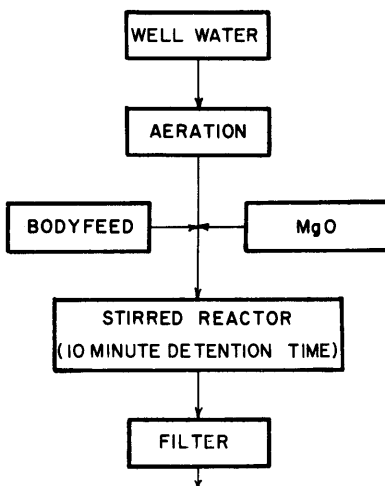


FIG. 1.—FLOW DIAGRAM FOR THE REMOVAL OF IRON USING CALCINED MAGNESITE

(MgO) and diatomaceous earth filter aid to aerated iron-bearing ground waters. Following a 5-min to 10-min period of intensive agitation, the water is filtered through either a gravity or pressure diatomaceous earth filter. The addition of small amounts of MgO to the filter precoat insures effective initial removal of iron in a freshly coated filter. The process has been found to be effective over a broad pH range (five to nine), requiring from 2 mg to 4 mg of MgO per mg of ferrous iron initially present in the raw water. The required dosages of MgO, normally 5 mg per l to 10 mg per l, increase if carbon dioxide or hydrogen sulfide are also present in the raw water. Fig. 1 is a flow diagram for the iron removal process.

Composition and Properties of Calcined Magnesite.—Calcined magnesite

is widely used in the ceramic industry as a catalyst and refractory. It is also used as a fuel oil additive and anticoking agent. Little information is available concerning the interaction of magnesium oxide with metal ions in aqueous solution. The type of magnesite used in the current studies was Type L-2-65

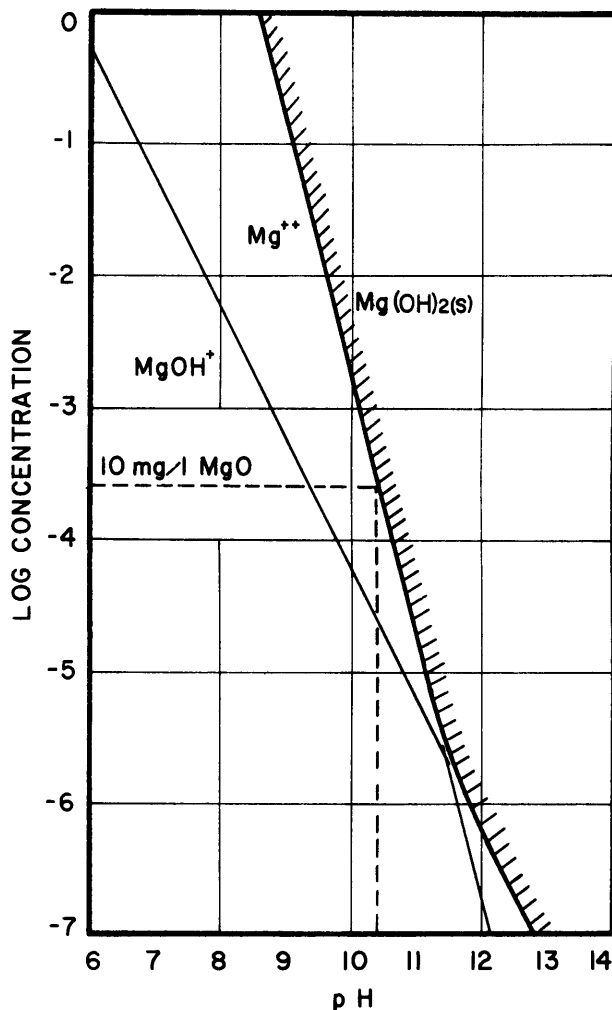


FIG. 2.—LOG CONCENTRATION—pH DIAGRAM FOR $Mg(OH)_2$ SOLUBILITY

Hammermilled Calcined Synthetic Magnesite, produced by Dow Chemical Company. The following are Dow's specifications for the material:

MgO (as is basis), min.	92.0 %
MgO (ignited basis), min.	95.0 %

Total impurities (ignited basis), max.	5.0 %
CaO (ignited basis), max.	1.7 %
NaCl (ignited basis), max.	0.7 %
Ignition loss (950° C)	1.5-5.0 %
Wet screen analysis	
Through 200 mesh, min.	80.0 %

Description: A technical grade of chemically active magnesia in the form of a white to pinkish white powder, bulk density about 20 u per cu ft to 25 lb per cu ft.

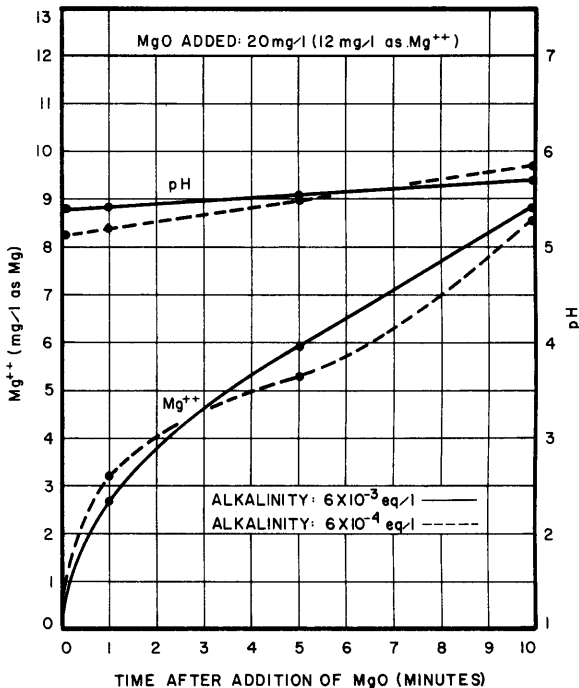


FIG. 3.—SOLUTION OF MgO EFFECT OF ALKALINITY AT LOW pH

Solubility of Magnesium Oxide.—The equilibria which govern the solubility of MgO in aqueous solution are listed in the following:

Reaction	pk (25° C)
$\text{MgO(s)} + \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2\text{(s)}$	5.4
$\text{Mg(OH)}_2\text{(s)} \rightleftharpoons \text{Mg}^{++} + 2\text{OH}^-$	10.8
$\text{MgOH}^+ \rightleftharpoons \text{Mg}^{++} + \text{OH}^-$	2.6

The log concentration—pH diagram for Mg(OH)_2 solubility, Fig. 2, shows that up to 10 mg per l MgO ($2.5 \times 10^{-4}\text{M}$) will dissolve completely if the pH is less than 10.5. Therefore, under ordinary circumstances, the addition of

magnesium oxide to ground waters should ultimately result in the complete solution of the MgO.

Effect of Solution of Magnesium Oxide.—The addition of dry magnesium oxide to water results in the formation of a suspension of MgO which gradually undergoes hydration and solution. The suspension may have surface properties which result in: (1) Adsorption of FeII; (2) destabilization of colloidal iron; or (3) accelerated oxidation of FeII at the MgO surface. Conversely, the solution of MgO will result in: (4) Increased pH; and (5) a small increase in the magnesium ion concentration.

Rate of Solution of Magnesium Oxide.—As no information was available

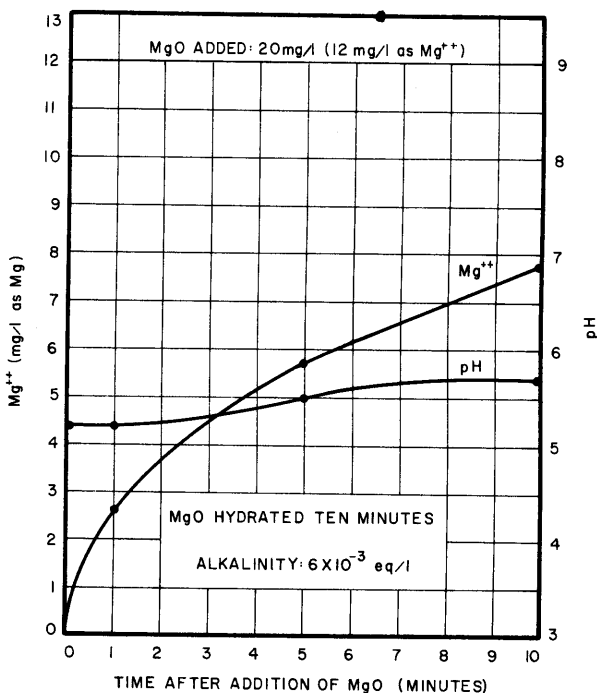


FIG. 4.—SOLUTION OF HYDRATED MgO

concerning the rate of solution of MgO and its effect on the pH of waters buffered by the carbonic acid system, studies were made of the change in pH and magnesium ion concentrations at room temperature when dry magnesium oxide was added to waters of various pH and alkalinity. Mixing was provided by a magnetic stirrer and conditions of mixing were held fairly constant. Figs. 3 to 6 show the results.

Fig. 3 shows the effect of alkalinity on the solution of 20 mg per l MgO at pH between five and six. Little difference was observed in the rate of solution at two levels of alkalinity as almost three-fourths of the MgO was dissolved in 10 min. As expected, the pH increase was less at the higher alkalinity.

Fig. 4 shows the rate of solution when the initial pH was between five and

six and the water had an alkalinity of 6×10^{-3} eq per l (300 mg per l CaCO_3 equivalent). This repeated the test represented in Fig. 3. In this instance, however, the MgO was hydrated (wetted) for 10 min before being added to the stirred reactor. The result was similar to that obtained when the MgO was added dry.

The effect of pH on the rate of MgO solution was explored and the results are shown in Fig. 5. For an initial alkalinity of 6×10^{-3} eq per l and initial pH reactions of 6.1 and 7.3, the rate of solution is seen to be similar to the rates obtained at pH 5.2 (Figs. 3 and 4).

Fig. 6 shows the rate of solution at pH 8.1 for two different alkalinities. At the higher alkalinity, the rate of MgO solution approximated the rates al-

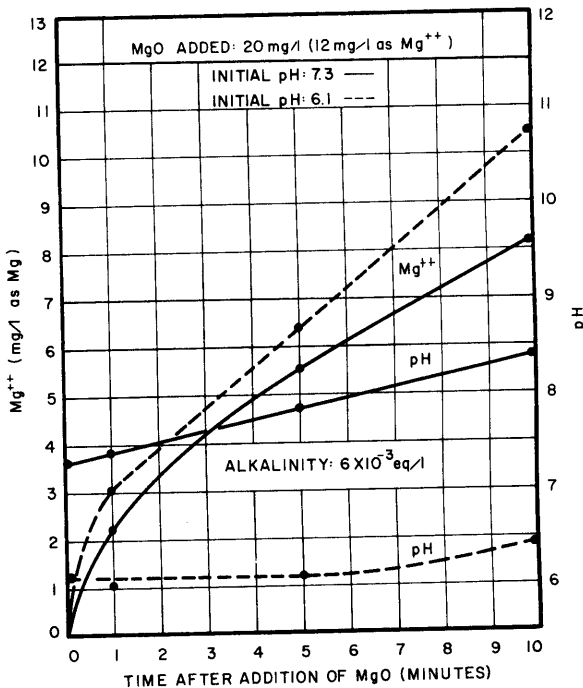


FIG. 5.—SOLUTION OF MgO EFFECT OF pH

ready observed. However, at the lower alkalinity, the solution of MgO was seen to increase the pH steadily owing to the low base-neutralizing capacity of this water. As the pH increased, so that the limit of MgO solubility was approached, the rate of solution of MgO was found to decrease.

MgO was found to dissolve slowly even with vigorous stirring using a laboratory magnetic stirrer. Over a wide range of pH and alkalinity, its solution was roughly 3/4 complete in 10 min, the mixing time generally provided in the calcined magnesite process for iron removal.

Surface Properties of Magnesium Oxide.—Although the presence of magnesium oxide in suspension is transient, its surface properties and slow dis-

solution may be extremely important factors in influencing precipitation and and destabilization in the short detention time provided during treatment for iron removal. Clearly, the hydrated MgO particle must have an abundance of attached hydroxyl groups on its surface.

Measurements of the electrophoretic mobility of MgO particles indicates that MgO has a very high negative charge. This charge is found to become only slightly less negative as iron removal proceeds (1).

In the diffusion layer surrounding the particle, there must be an excess of hydroxyl ions formed as a result of the solution of the MgO. In this region of high pH, the rate of iron oxidation may be considerably enhanced since it increases in proportion to the square of the hydroxyl ion concentration (7).

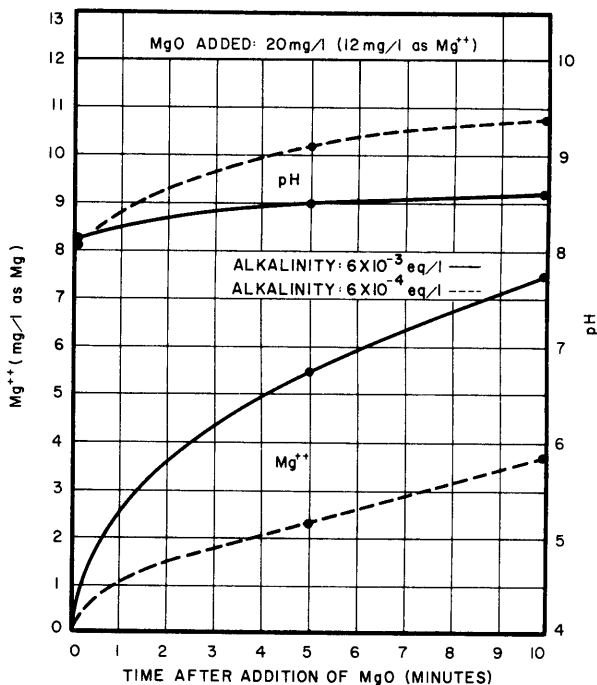


FIG. 6.—SOLUTION OF MgO EFFECT OF ALKALINITY AT HIGH pH

Moreover, ferrous hydroxide and ferrous carbonate could precipitate at the pH found in the region close to the surface of magnesium oxide particles. A hypothetical model of conditions existing in the liquid film near a magnesium oxide particle is shown in Fig. 7. From the model it would appear that there must be an optimal rate of stirring which would promote iron precipitation. Increased stirring rates would increase the opportunity to bring ferrous ions into the liquid film where the precipitation would take place. However, increased stirring rates would also tend to decrease the film thickness, thereby reducing the volume of the region in which reaction might take place.

Reactions in the liquid film may be influenced by substances which influ-

ence the rate of solution of MgO. Hydrogen sulfide (H_2S) might influence the solution of MgO by forming a surface coating of MgS. The deposition of precipitates of iron and manganese might also influence the surface properties

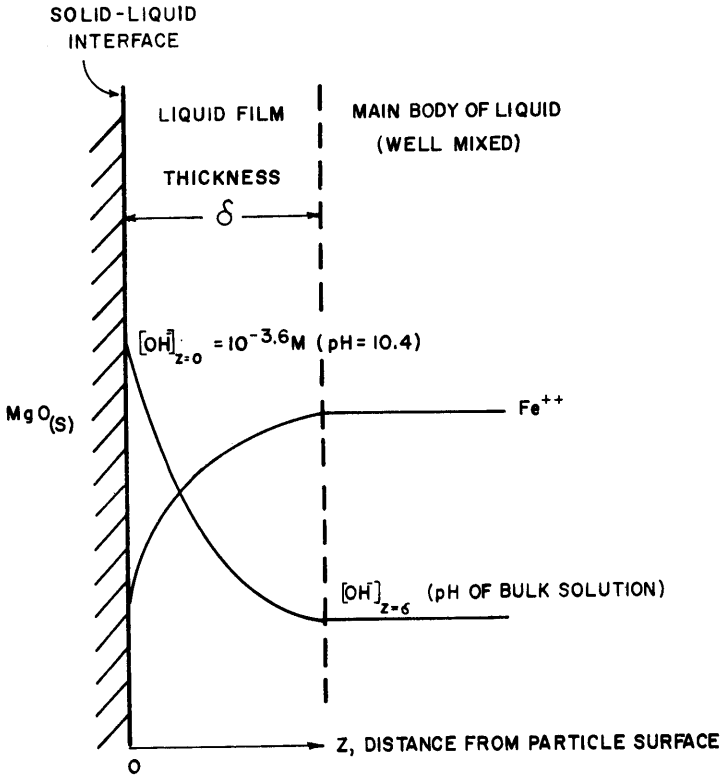


FIG. 7.—MODEL OF CONCENTRATION PROFILES IN LIQUID FILM ADJACENT TO MAGNESIUM OXIDE PARTICLE

and rate of solution of the magnesium oxide. Substances which would react with hydroxyl ion would be expected to slow the precipitation reaction.

STUDIES OF IRON PRECIPITATION

Laboratory experiments were conducted on the precipitation and oxidation of ferrous iron following the addition of MgO. Batch studies were carried out in stirred reactors. Buffering was provided by the addition of $NaHCO_3$ to yield an alkalinity of approximately 6×10^{-3} eq per l. Oxygen was stripped from the water prior to the addition of ferrous iron and the pH adjusted by controlling the ratio of CO_2 and N_2 in the mixture of gases bubbled through the test solution. Generally, about 5 mg per l of Fe was added to the test solution. Efforts were made to follow both iron oxidation and precipitation fol-

lowing the addition of MgO. A control reactor, without MgO, was run parallel to each test.

Analytic procedures for ferrous iron are not clearly defined or widely accepted, especially in systems which contain incipient precipitates of hydrous ferric oxides. However, the progress of oxidation was followed by determining ferrous iron in unfiltered samples using the bathophenanthroline reagent. The precipitation of iron was estimated by determining both total and ferrous iron on samples filtered through a 0.45μ membrane filter. Samples for ferrous iron were acidified and treated with an acetic acid (pH 4.0) buffer and the colorimetric reagent, bathophenanthroline (5). The ferrous-bathophenanthroline complex was then extracted with isoamyl alcohol and made up to volume with ethyl alcohol for colorimetric analysis. Samples for total iron were analyzed using the orthophenanthroline procedure for total iron as described in Standard Methods (6).

The procedures followed in the experiments were essentially the following: the test water was purged with nitrogen until the dissolved oxygen was

TABLE 1.—RESULTS OF STUDIES OF IRON PRECIPITATION

TEST 2		Initial Conditions		
	Fe: ≈ 2 mg/l	Alkalinity:	9×10^{-3} eq/l	
	DO: < 0.1 mg/l	pH: 6.9	Temp.: 25°C	
(a) No MgO	TIME, MINUTES	<u>1</u>	<u>5</u>	<u>10</u>
	FeII	-	1.7	1.8
	FeII _f	-	1.2	1.5
	pH	6.9	6.9	6.9
(b) 20 mg/l MgO	FeII	1.6	1.6	1.6
(5×10^{-4} M)	FeII _f	1.2	0.8	0.9
(12 mg/l Mg ⁺⁺)	Mg ⁺⁺	7	8	8
	pH	6.9	-	7.2
TEST 3		Initial Conditions		
	Fe: ≈ 5 mg/l	Alkalinity:	6×10^{-3} eq/l	
	DO: < 0.1 mg/l	pH: 6.9	Temp.: 25°C	
(a) No MgO	TIME, MINUTES	<u>1</u>	<u>5</u>	<u>10</u>
	Fe	5.0	-	-
	FeII	5.2	5.2	5.2
	Fe _f	4.3	-	4.2
	FeII _f	-	-	3.9
	pH	6.9	6.9	7.0
(b) 20 mg/l MgO	Fe	4.6	-	-
	FeII	4.3	4.6	4.5
	Fe _f	2.6	3.6	1.8
	FeII _f	-	-	2.0
	Mg ⁺⁺	2.9	4.8	5.5
	pH	7.1	7.2	7.4

TABLE 1.—CONTINUED

TEST 4		Initial Conditions			
		Fe: ≈ 5.0 mg/l DO: < 0.1 mg/l	Alkalinity: 6×10^{-3} eq/l pH: 5.7	Temp.: 24°C	
(a) No MgO	TIME, MINUTES		<u>1</u>	<u>5</u>	<u>10</u>
Stirred, open to atmosphere	Fe _f	-	5.5	5.6	
	pH	5.7	5.7	5.85	
	DO	-	1.6	2.2	
(b) 20 mg/l MgO	Fe	5.0	-	-	
Stirred, open to atmosphere	Fe _f	-	4.8	-	
	FeII _f	-	5.3	5.0	
	pH	5.8	-	-	
	DO	1.0	1.2	2.9	
	Mg ⁺⁺	3.9	5.8	7.7	
(c) Aerated prior to addition of 20 mg/l MgO	Fe	5.5	-	-	
	Fe _f	4.75	-	1.3	
	FeII _f	-	-	1.7	
	pH	5.6	5.7	5.7	
	DO	5.2	4.9	5.3	
TEST 5		Initial Conditions			
		Fe: 6.0 mg/l DO: 7.8 mg/l	Alkalinity 6.8×10^{-4} eq/l pH: 5.4	Temp.: 25°C	
(a) No MgO	TIME, MINUTES		<u>1</u>	<u>5</u>	<u>10</u>
	FeII	6.0	5.9	-	
	FeII _f	-	6.0	5.9	
	DO	7.7	7.8	7.8	
	pH	5.5	5.5	5.5	
(b) 20 mg/l MgO	FeII	-	0.2	0.3	
	FeII _f	1.7	0.5	0.5	
	DO	7.7	7.4	7.4	
	pH	5.6	6.2	6.1	

less than 0.1 mg per l; the flow of carbon dioxide was then adjusted until a steady-state pH was achieved; when the liquid volume was small, equilibration occurred after a few minutes. Iron was added as ferrous chloride in hydrochloric acid solution; thereafter, samples were drawn for analysis for total iron, (Fe) and ferrous iron, (FeII) on both unfiltered and membrane filtered, (Fe_f, FeII_f) aliquots. Initially, all of these values should have been roughly equal, indicating that all of the iron was in the ferrous form and was filtrable.

With the test solution thus prepared, three portions were drawn into stoppered BOD bottles as controls while another three portions were drawn into

TABLE 1.—CONTINUED

TEST 6		Initial Conditions		
		Fe: 6.1 mg/l	Alkalinity: 5×10^{-3} eq/l	
		DO: < 0.1 mg/l	pH: 6.1	Temp.: 25°C
(a) No MgO	TIME, MINUTES	<u>1</u>	<u>5</u>	<u>10</u>
	Fe	5.6	6.1	5.6
	FeII	6.4	6.3	6.3
	Fe _f	5.3	5.6	5.3
	FeII _f	6.0	6.0	6.0
	pH	6.1	6.1	6.1
(b) 20 mg/l MgO	Fe	5.9	6.7	6.2
	FeII	5.4	5.4	5.4
	Fe _f	3.8	4.0	3.9
	FeII _f	-	4.3	4.2
	pH	6.1	6.1	6.1
	Mg ⁺⁺	1.2	2.4	-
(c) No MgO (aerated)	Fe	5.9	5.6	6.1
	FeII	3.8	2.2	0.9
	Fe _f	4.8	2.2	-
	FeII _f	3.8	2.2	0.8
	pH	6.3	6.3	6.4
	DO	7.3	7.4	7.5
(d) Aerated prior to addition of 20 mg/l MgO	Fe	5.0	5.6	5.3
	FeII	1.0	0.2	0.0
	Fe _f	1.0	0.2	0.2
	FeII _f	1.0	0.0	0.1
	pH	6.3	6.8	6.9
	DO	7.5	7.1	7.9
	Mg ⁺⁺	2.9	5.0	6.2

All values reported as mg/l except pH

Fe = total iron present in reactor = FeII + FeIII

Fe_f = total iron capable of passing through membrane filter

FeII = total ferrous iron present in reactor

FeII_f = ferrous iron capable of passing through membrane filter

BOD bottles containing dry MgO. The contents of each bottle were stirred. Individual bottles were opened and sampled at intervals of 1 min, 5 min, and 10 min after the portion was drawn to initiate the test. The results of the experiments are tabulated in Table 1.

ANALYSIS OF RESULTS

Test 1.—Within 5 min following the addition of FeCl₂ to the test solution, the iron in filtered samples was found to be approximately zero. This indi-

