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| 13. ABSTRACT (Maximum 200 words)<br>DURING EXPERIMENTAL TREATMENT OF GROUND WATER FROM WELL 118 WITH ULTRAVIOLET LIGHT AND OZONE (UV/O <sub>3</sub> ), PRECIPITATION OF IRON AND MANGANESE OXIDES OCCURRED. THE OXIDES WERE FOUND TO INTERFERE WITH THE PROCESS BECAUSE OF THEIR OPACITY. THE POSSIBILITY OF REMOVING IRON AND MANGANESE IN A FEEDWATER PRETREATMENT PROCESS HAS BEEN INVESTIGATED. THE PROCESS ENVISIONED WOULD HAVE UTILIZED THE UNREACTED OZONE VENTED FROM THE UV/O <sub>3</sub> PROCESS; OTHER OXIDIZING AGENTS WERE NOT CONSIDERED BECAUSE OF THEIR HIGHER COST RELATIVE TO THE OZONE AVAILABLE IN THE VENT GAS. ALTHOUGH THE PRETREATMENT PROCESS IS TECHNICALLY FEASIBLE, SEVERAL TANK-AGITATOR SETS WOULD BE REQUIRED IN CONJUNCTION WITH A VENT GAS COMPRESSOR AND AUXILIARY INSTRUMENTATION. INSTEAD OF THE PRETREATMENT PROCESS, A SIMPLER SCHEME IS PROPOSED THAT WOULD CONSIST ONLY OF A RECIRCULATION LOOP THROUGH A FILTER. FLUID FROM THE UV/O <sub>3</sub> UNIT WOULD BE FILTERED AND RETURNED TO THE UNIT SO THAT SUBSTANTIALLY ALL THE PRECIPITATES WOULD BE REMOVED AS FORMED; OPTICAL TRANSPARENCY AND OXIDATION EFFICIENCIES WITHIN THE UV/O <sub>3</sub> UNIT COULD THUS BE |  |                                             |  |                                                                   |  |
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**FINAL REPORT**  
**IRON AND MANGANESE REMOVAL BY OXIDATION**

REPORT No. 10557-5  
UNDER WORK STATEMENT OF JAN. 1978 FOR  
RESEARCH SERVICES, ITARMS No. 1.05.11

CONTAMINATION CONTROL DIRECTORATE  
Rocky Mountain Arsenal  
Commerce City, Colorado 80022

Providing Research Services For

Waterways Experiment Station  
Vicksburg, Mississippi 39180

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ITARMS TASK NO. 1.05.57  
(See March 1978 RMA Progress Report and MES Test  
Plan Jan. 1978, Previous ITARMS No. 1.05.11)

AUGUST 1978

Process Development & Evaluation Division  
Contamination Control

C. Loven, Chief  
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SUMMARY:

During experimental treatment of groundwater from Well 118 with Ultra Violet Light and Ozone (UV/O<sub>3</sub>), precipitation of iron and manganese oxides occurred. The oxides were found to interfere with the process because of their opacity.

The possibility of removing iron and manganese in a feedwater pretreatment process has been investigated. The process envisioned would have utilized the unreacted ozone vented from the UV/O<sub>3</sub> process; other oxidizing agents were not considered because of their higher cost relative to the ozone available in the vent gas.

Although the pretreatment process is technically feasible, several tank-agitator sets would be required in conjunction with a vent gas compressor and auxiliary instrumentation. Instead of the pretreatment process, a simpler scheme is proposed that would consist only of a recirculation loop through a filter. Fluid from the UV/O<sub>3</sub> unit would be filtered and returned to the unit so that substantially all the precipitates would be removed as formed; optical transparency and oxidation efficiencies within the UV/O<sub>3</sub> unit could thus be maintained with considerably less equipment than the ozone pretreatment process would require.

A filter-pump combination is on hand and will be tested when the UV/O<sub>3</sub> equipment assembled by WES (Waterways Experiment Station) reaches RMA in early October.

## OXIDATION PROCESSES FOR REMOVING IRON AND MANGANESE FROM RMA GROUNDWATER

### Introduction:

Iron and manganese are present in the groundwater at RMA. A sample well (Well 118) near Basin F has been found to contain about 26ppm manganese and about the same of iron although the Basin contains less than 0.1 ppm manganese and only about 6 ppm iron. Water dissolves manganese and iron during its passage from the surface through permeable ground structures.

Well 118 is a comparatively highly contaminated water source but is otherwise representative of RMA groundwater; a successful treatment process for Well 118 would be adaptable to the other RMA waste water locations.

This report recognizes two criteria controlling manganese levels; iron levels are of secondary concern because iron is easier to oxidize than manganese. To meet potable water standards, manganese levels below .05ppm are required (Ref. 1). For the feed to a water treatment process, higher residual manganese levels would probably be acceptable. As an estimate, the UV/O<sub>3</sub> process could tolerate one or two ppm manganese, corresponding respectively to conversion levels of 96% and 92% of the original manganese concentration.

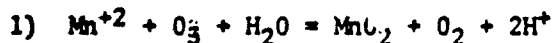
These two criteria have a major effect on an oxidative process design because the .05ppm level requires a high manganese conversion level (99.8%) that in turn requires large reactors; when conversion levels are reduced a few percent, the manganese oxidation reactor can be disproportionately smaller.

At the present time, the process under consideration is treatment of feed water for the UV/O<sub>3</sub> oxidation reactor. The objective in oxidizing the manganese is to prevent its interference with the UV/O<sub>3</sub> process; UV light

is blocked if significant amounts of the manganese oxide precipitate are allowed to form or accumulate within the UV/O<sub>3</sub> apparatus.

There are several chemical reactions that produce highly insoluble manganese and iron compounds.

Oxidation Reactions:



The oxidizing agents are ozone (reaction 1) and hypochlorite (reaction 2); both produce manganese dioxide from soluble manganese compounds. Manganese dioxide is slightly soluble, and its solubility varies with pH (Ref. 2).

TABLE 1 (See p. 40 Ref. 2)

| pH  | Solubility MnO <sub>2</sub><br>ppm | pH   | Solubility MnO <sub>2</sub><br>ppm |
|-----|------------------------------------|------|------------------------------------|
| 2.1 | 1.3                                | 7.0  | 0.1                                |
| 3.0 | 0.9                                | 8.4  | 0.3                                |
| 5.4 | 0.5                                | 8.7  | 0.02                               |
| 6.9 | 0.1                                | 10.2 | 0.1                                |
|     |                                    | 10.6 | 0.2                                |

The data in the table above points out the necessity to control pH at about seven or above if levels of dissolved manganese (IV) are to be held below 1ppm. *all but pH 2.1 is below 1ppm.*

Precipitation as the Hydroxide:

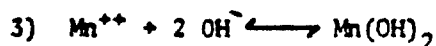


TABLE 2 (p. 5 Ref. 2)

Solubility of Manganese (II)

| pH | ppm Mn <sup>++</sup>   |
|----|------------------------|
| 7  | 5.5 X 10 <sup>5</sup>  |
| 8  | 5.5 X 10 <sup>3</sup>  |
| 9  | 5.5 X 10 <sup>1</sup>  |
| 10 | 5.5 X 10 <sup>-1</sup> |
| 11 | 5.5 X 10 <sup>-3</sup> |

At the higher pH levels, the manganese (II) in solution is comparable to the manganese (IV) solubility. Conditioning of feed water by reaction (3) is feasible.

In practice, when ground water is adjusted to the high pH levels, calcium and magnesium hydroxides precipitate simultaneously with iron and manganese, and a gelatinuous sludge must be disposed of. The precipitate has the advantage that it adsorbs fluoride ion and thus removes a substantial part of the fluoride from solution.

In contrast, oxidation produces a fine suspension, consisting only of iron and manganese oxides, that has only a fraction of the volume of the hydroxide sludge. Although the oxide suspension has a very slow sedimentation rate and must be filtered to obtain reasonable throughput rates, there is a considerably smaller amount of solids for disposal because the calcium and magnesium remain in solution.

This report has been confined to a study of the ozone oxidation (reaction 1 above), although the sodium hypochlorite oxidation is at least equally effective. Vent gas from the UV/O<sub>3</sub> reactor will provide a source of ozone that otherwise would be wasted. In this sense the ozone for manganese oxidation is free and the hypochlorite reaction becomes relatively expensive. This consideration also bears on the hydroxide feed treatment above because the unreacted ozone is not utilized to precipitate iron and manganese as hydroxides. Since ozone is unstable, recovery of unreacted ozone is not feasible. Thus, if the hydroxide feed treatment is adopted, special efforts to utilize all the ozone for oxidation of organics will be necessary. This is an important reason for treating ozone utilization efficiency as a significant variable in the UV/O<sub>3</sub> process.

As preliminary studies, manganese oxidation tests with air and pure oxygen were carried out. The data is presented but ozone was the only effective oxidant tested. Hypochlorite is known to be effective (Ref. 2) but its behavior in RMA waters has not been tested because of the ozone availability; formation of undesirable chlorinated organic compounds has been an additional factor tending to exclude the hypochlorite oxidation process.

Analysis of the iron and manganese oxidation rates was based on the following equation which states that the rate of oxidation is proportional to the product of the concentrations of oxidant and manganese.

$$(I) \quad \frac{-dc_1}{dt} = KC_2 C_1$$

Where K = Rate constant

$C_2$  = Concentration of the oxidizing agent

$C_1$  = Concentration of manganese

( $C_1$  may also represent iron, for iron oxidation)

In practice,  $C_2$  is proportional to the mole-fraction of oxidant in the gas phase that is bubbled through the reaction mixture. Other factors affecting  $C_2$  are (a) the rate of diffusion of the oxidant from the gas phase into the liquid phase (the diffusion rate is strongly influenced by the degree of agitation), (b) the rate of reaction with manganese, and (c) for ozone, its rate of decomposition.

It was found that the product  $KC_2$  could be treated as a pseudo first order rate constant for most of the reaction data. The pseudo rate constant is symbolized by K in the remainder of this report. It is recognized that values of K obtained are approximate because of the neglect of the above side reactions, but reaction time estimates so derived will be accurate enough for preliminary design estimates.

From Equation I, if  $KC_2 = K_p = K$

$$(II) \quad \ln \frac{C_0}{C} = K(t - t_0)$$

Values of K reported herein were obtained from the experimental data by means of Equation II.

This is the final report dealing with feed preparation for the UV/O<sub>3</sub> process. A preliminary report was published March 78 (Ref. 1).

#### Experimental:

Preliminary oxidation tests with air and pure oxygen were carried out to establish the degree of manganese/iron oxidation. A vertical tube reactor was equipped with a gas sparger to produce a stream of small bubbles. The bubbles caused some agitation as they rose through the reactor. Table I illustrates that the reactor caused rapid solution of oxygen from air; tap water was saturated in less than 15 minutes.

The waste waters all contain organic compounds as well as iron and manganese. Since any loss of these compounds by volatilization would appear to be due to oxidation, an estimate of the volatilization losses with nitrogen was developed. Nitrogen was fed to the reactor in place of an oxygen containing gas. After six hours nitrogen feed, volatilization was assumed to be complete and the nitrogen was replaced with air for a period of 21 hours. Next, pure oxygen was introduced for four hours. The results of these experiments are listed in Table II.

In general, the only organic compound volatilized was DCPD. Analysis of DCPD at ppb levels is difficult and the results in Table II are erratic, but volatilization appears to have been rapid until levels of 20 to 30 ppb were reached.

The loss of manganese during sparging with nitrogen is an anomalous result that would require more experimentation for a complete explanation. It was not encountered in tests with air (which is 30% nitrogen) or oxygen, and was not examined further. Treatment with air or oxygen provided only



an extremely slow removal of manganese. A rate constant estimate is  $5.5 \times 10^{-4} \text{ Min}^{-1}$  for air, but the analytical uncertainty for manganese is comparatively large in the ppm range as indicated by comparing rate estimates; essentially equal constants for oxygen and air were calculated from the data in Table II, but a ratio of about five is the expected result because of oxygen concentration differences between air and pure oxygen.

*O<sub>2</sub> in air 21%  
O<sub>2</sub> pure 100%*

One possibility for the lack of manganese oxidation is the possible competition for oxygen from the organic matter present. COD analyses are erratic and do not exclude this possibility.

A carbon column was used to adsorb organics and the product was treated with air and oxygen with results given in Table III and Table IV. Carbon treatment reduced the COD analyses from about 450ppm (Table II) to about 200ppm (Tables III and IV). The rate constant for air was estimated at  $5.4 \times 10^{-4}$ , indicating the same chemistry as in Table II, before carbon treatment. With oxygen, more data than that in Table II was obtained and the rate constant was more accurate. The average was  $3.75 \times 10^{-3}$ . This value is 6.9 times as large as the oxidation rate for manganese with air. Air is near 20% oxygen so that a rate increase of 5 would be expected for oxidation with pure oxygen. Within experimental error, the increase is as expected ( $7.5 \times 10^{-4}$  instead of  $5.5 \times 10^{-4}$  for air would have been exactly as expected).

The COD results confirmed the absence of oxidation of dissolved organics for both air and oxygen. Thus, the extremely slow oxidation rate for manganese is characteristic of its chemistry and is not due to interference from the organic compounds present.

Iron was absent from Well 118 water after the carbon treatment and was at very low levels without the treatment. The well water was known to contain iron, and iron was detected in the samples after the air cushion in the surge tank for the well was flushed with nitrogen. Greater care in pH adjustment of samples was instituted at the same time. Table V shows 44.7ppm iron and Table VI shows 25 and 18ppm iron, prior to oxidation. Comparable variation among the manganese analyses indicates that some unidentified variable affected both analyses, but substantial iron levels were present.

Contrary to air and oxygen, ozone produced significant oxidation of manganese. Table V shows rate constants obtained with air feed to the ozonizer; Table VI has constants from oxygen feed. Pure oxygen feed produces a greater concentration of ozone and correspondingly higher (pseudo) rate constants. The two are  $9.4 \times 10^{-3}$  and  $5.4 \times 10^{-2}$ ; the ratio is about 5.7, indicating the same increase in ozone concentration with pure oxygen compared to air. As for the previous rate constant ratio, this is approximately what would be expected from the oxygen concentration in air and pure oxygen. Table VI also illustrates the importance of agitation in obtaining faster oxidation rates.

When Well 118 water was treated with carbon, a clear, color-free product was obtained in which a precipitate was easily observed. Advantage was taken of this property by adding caustic and measuring the calcium and magnesium hydroxide sedimentation rate. The data is summarized in Figure I; about four hours settling time for a 54-inch liquid depth would be required for clarification by hydroxide formation and sedimentation.

In contrast to hydroxides, the iron and manganese oxides formed fine precipitates with extremely slow sedimentation rates; filtration appeared

to be the best clarification technique. Diatomaceous earth was found to be  
a useful filter-aid.

DEPA?

### Discussion:

The rate constant values from Table VI can be used to estimate reactor volume requirements for various feed rates. In this connection, equations were developed for three reaction models.

#### Model (I) - Batch Reaction

For this model, a reactor is filled with water to be treated and stirred continuously; water is neither added or removed. At a fixed reaction temperature, the oxidizing gas is dispersed in small bubbles throughout the reactor so that K is maximum. Agitation and gas feed are maintained until the desired degree of conversion is obtained.

The equation for this reaction model is:

$$(II) \quad \ln (C_0/C) = K (t_2 - t_1)$$

Where K = pseudo first order rate constant ( $\text{min}^{-1}$ )

$C_0$  = concentration of oxidizable material (manganese or iron) at time  $t_1$  (min.)

C = concentration at time  $t_2$  (min.)

This reaction model corresponds to the experimental method for measuring the K values listed in the Tables.

#### Model (II) - Single Stage Continuous Reaction

For this model, there is a continuous water feed and a volumetrically equal withdrawal so that the reactor remains full. Continuous oxidant feed and agitation are provided as in Model I. Under this condition, starting with a reactor full of untreated water, the manganese or iron content of the reactor (or of the effluent) drops to a minimum, substantially constant level, over a period of time.

The equation describing this model is:

$$(III) \quad C/C_0 = \frac{G + KV e^{-(K + \frac{G}{V})t}}{G + KV} \quad \text{ref.}$$

Where:  $t$  = running time since reaction started (min.)  
 $G$  = feed (and effluent) rate (gpm)  
 $V$  = reactor volume (gal.)  
 $C_0$ ,  $C$ , and  $K$  = same as above

In terms of conversion:

$$(III-A) \quad \% \text{ conversion} = 100 \left\{ \frac{KV \left[ 1 - e^{-(K + \frac{G}{V})t} \right]}{G + KV} \right\}$$

From (III-A), as  $t$  becomes large (several hours) the % conversion approaches a steady level.

From (III) above:

$$(IV) \quad C/C_0 = \frac{G}{G + KV}$$

From (III-A) above:

$$(IV-A) \quad \% \text{ Conversion} = \frac{KV}{G + KV}$$

Equation (IV-A) may be solved to express  $V$  in terms of the desired conversion (see Table VII).

#### Model III - Multiple Staged Continuous Reactor

In this model, a series of Model II reactors is set up so that the effluent of Stage (N-1) becomes the feed to Stage N.

As shown in Table VI, for high conversion levels, a single stage reactor becomes very large. Staging is a way to reduce the large volume requirements of the single stage reactor. Note from (III-A) and (IV-A) that the % conversion is independent of the concentration of reactive material in the feed stock. Assume each stage provides 40% conversion; the accumulative conversion then increases as follows:

| <u>Stage No.</u> | <u>Accumulative Conversion</u>   |
|------------------|----------------------------------|
| 1                | 40%                              |
| 2                | $40\% + .4(100-40) = 64\%$       |
| 3                | $64\% + .4(100-64) = 78.4\%$     |
| 4                | $78.4\% + .4(100-78.4) = 87.0\%$ |

These calculations are easily generalized for other conversion levels and other numbers of stages.

By using the above equation, the total volume of N stages can be compared with the volume of a single stage continuous reactor, for a given conversion level. As an exercise, these calculations have been made in Table VII and graphed in Figure 2. At the higher conversion levels, the reactor volume for N stages is only a few percent of the single stage volume. The exercise in Table VII assumed a 50gpm feed rate; reactor volumes for other feed rates can be calculated by the formula below:

$$(V) \quad V^1 = G/50 V_c \quad \text{Where: } G \text{ is the new feed rate}$$

Where:

$V^1$  is the desired reactor volume

G is the new feed rate

$V_c$  is the reactor volume from Table VII (either single or multiple stage volume)

Using Equation II (Model I), the oxidation rates for iron and manganese can be compared under different reaction conditions:

#### OXIDATION AT ONE ATMOSPHERE AND AMBIENT TEMP.

| <u>Oxid. Agent</u>                      | <u>Best Estimate of K</u> |                      | <u>K From Table</u> | <u>Agitation</u> |
|-----------------------------------------|---------------------------|----------------------|---------------------|------------------|
|                                         | <u>Fe</u>                 | <u>Mn</u>            |                     |                  |
| Air                                     | --                        | $5.5 \times 10^{-4}$ | II & III            | From Sparger     |
| 100% Oxygen                             | --                        | $3.8 \times 10^{-3}$ | IV                  | " "              |
| O <sub>3</sub> from Air                 | $1.4 \times 10^{-2}$      | $6.2 \times 10^{-3}$ | V                   | " "              |
| O <sub>3</sub> from 100% O <sub>2</sub> | $1.3 \times 10^{-1}$      | $1.3 \times 10^{-2}$ | VI                  | " "              |
| O <sub>3</sub> from 100% O <sub>2</sub> | 1.2                       | $5.4 \times 10^{-2}$ | VI                  | Sparger & Pump   |

Using the above values for K, the increase in reaction rates from air through ozone is apparent; the oxidation rate with ozone and good agitation is about 100 times the rate with air.

An increase in K is observed when agitation is increased by addition of a pump for recirculation; compare ozone with and without the pump.

The maximum value of K above is a reasonably good estimate of the best value to be expected in a large scale unit. In practice vented ozone from the UV/O<sub>3</sub> process would be used; its concentration would be approximately the same as that generated in the above tests because the ozone reaction efficiency in the UV/O<sub>3</sub> process is comparatively low; most of it passes unchanged through the UV/O<sub>3</sub> reactor. It follows that K will be similar for the two cases.

A further chemical consideration is that iron reacts preferentially with the ozone; manganese oxidation doesn't reach measurable rates until nearly all the iron has been oxidized. Iron concentration in Well 118 appears to be comparable to the manganese concentration and this additive effect essentially doubles the ozone consumption that would have been needed for manganese alone.

The efficient utilization of ozone is an important design feature. In Reference (2) an estimate of 50% of the ozone feed was given as maximum utilization efficiency for ozone in the oxidation of manganese, although levels of 2 or 3% were typical of laboratory results. The higher figure was an estimate by industry for a well designed plant and was probably optimistic. All of this information indicates that high power input for agitators would be required in an operating plant.

A second important design feature is the total reactor volume required for oxidation of the manganese. Data below was taken from Figure 2, using Equation (V) to convert the graphed data to the three feed rates shown.

# REACTOR VOLUMES

| Number<br>of<br>Stages | Feed Rates |     |            |        |            |        |
|------------------------|------------|-----|------------|--------|------------|--------|
|                        | 2gpm       |     | 166gpm     |        | 50gpm      |        |
|                        | Conversion |     | Conversion |        | Conversion |        |
|                        | 90%        | 95% | 90%        | 95%    | 90%        | 95%    |
| 1                      | 336        | 704 | 27,888     | 58,432 | 8,400      | 17,500 |
| 2                      | 160        | 260 | 13,280     | 21,580 | 4,000      | 6,400  |
| 3                      | 128        | 192 | 10,624     | 15,934 | 3,200      | 4,900  |
| 4                      | 116        | 170 | 9,628      | 14,110 | 2,900      | 4,150  |
| 5                      | 108        | 156 | 8,964      | 12,948 | 2,700      | 3,950  |

The 2gpm feed rate corresponds to the feed rate of the Bench Scale UV/O<sub>3</sub> Apparatus to be tested at RMA by NES. Based on the above calculations, a single stage reactor of approximately 700 gallons has been supplied to provide 95% conversion (oxidation). If staging were used, two 130-gal. reactors, or three 64-gal. reactors, etc., would provide the same degree of oxidation.

The 166gpm rate approximates the size of a field scale plant for water treatment. This size plant would require a 58,000-gal. tank for manganese oxidation if only one stage were used, but four 3,500-gal. tanks or five 2,600-gal. tanks in series would provide the same 95% degree of oxidation. Cost data for tanks of these sizes has not been obtained but 4 or 5 of the small tanks needed for staged operations would be considerably cheaper than the single 58,000-gal. tank. Since 166gpm is a large throughput, reactor volume estimates for 50gpm have also been developed.



The above size estimates are for the conversion percentages 90% and 95%, but as shown in Table VII and Figure 2, conversion levels between 95% and 100% call for disproportionately larger reactors. Accordingly, if high manganese conversion levels are required in a given application, because of either high concentration in the feed or extremely low concentrations in the product, oxidation with ozone may not be economical.

As an approximation of oxidation costs for manganese removal in an ordinary water treatment process, Figure 3 was taken from Reference 2. Costs for both ozone and sodium hypochlorite are shown. The basis for the cost estimates shown is somewhat different from the RMA situation.

#### OZONATION COST DATA BASIS

| <u>Reference 2</u>         |     | <u>RMA</u>                                              |
|----------------------------|-----|---------------------------------------------------------|
| Ozone Cost Charged         | (A) | Have Byproduct Ozone                                    |
| % Conversion Not Specified | (B) | High % Conversion Needed                                |
| No Iron Present            | (C) | Iron Equals Manganese                                   |
| Cost in 1974 Dollars       | (D) | Cost in 1980 Dollars                                    |
| 50% of Ozone Reactor       | (E) | Low % Ozone Reacts Because of Low Organic Concentration |

In view of the above differences in basis, ozonation costs for RMA would have to be developed specifically for RMA, if the pilot plant design is otherwise satisfactory. It is possible to estimate the cost of ozone consumed for oxidation of manganese and iron from Figure 3, if the capital cost of the Ozone Generator is entirely charged to the UV/O<sub>3</sub> process.

These estimates have been superimposed as dashed lines on Figure 3. At 5000gph, the indicated ozone cost is \$15.00 per day.

Conclusions and Recommendations:

*\* Where is a discussion of the two  
controlling criteria on p. 1.  
b) Removal to below suggested limits  
c) Removal to below level suitable  
for UV-O<sub>3</sub>*

(1) Ozone will oxidize manganese at a practical reaction rate; air or pure oxygen will not. All measures to increase ozone concentration in solution are important, such as agitation and the use of pure oxygen feed to the ozonizer. In principle, increased pressure would increase the oxidation rate but conventional means for such increase would probably not be economical. Iron present with manganese is preferentially oxidized and unavoidably consumes ozone. The data indicates that manganese and iron are oxidized much more rapidly than the organic matter present.

(2) When it is necessary to convert high percentages of manganese to its oxide, the required reactor volume becomes disproportionately large. Considerable reactor-volume reduction is possible by staging the oxidation in a series of comparatively small reactors, but conversion levels above 90% or 95% may not be feasible. Accordingly production of manganese levels much below 1ppm may not be feasible.

(3) There are alternative means of oxidizing manganese such as sodium hypochlorite, but this report has been confined to the ozone reaction because ozone is a byproduct of the UV/O<sub>3</sub> organic oxidation process, and because it does not produce undesirable byproducts such as chlorinated hydrocarbons.

(4) Iron and manganese can also be removed by a conventional lime-soda water treatment process; the sludge produced is suitable for landfill but is much greater in quantity than the iron and manganese oxides because it includes calcium and magnesium hydroxides. From the standpoint of iron and manganese removal, the process is suitable, but it might increase costs because it doesn't utilize the byproduct ozone. Since calcium and magnesium are not toxic, their removal may not be necessary from a water quality

standpoint, although the recommended total dissolved solids level of 500ppm is probably exceeded by the calcium and magnesium in some RMA groundwaters.

A ruling from the Colorado Public Health Service would be helpful in choosing between the two processes.

(5) The above considerations lead to the following recommendation of a greatly simplified design for the UV/O<sub>3</sub> process.

#### New Design to Replace UV/O<sub>3</sub> Feed Pretreatment

Equip the UV/O<sub>3</sub> reactor with a recirculating pump and filter so that opaque particles that form in the UV/O<sub>3</sub> reactor will be removed before they interfere significantly with UV light transmission. Diatomaceous earth has been found to be a suitable filter aid in experimental work.

Some advantages of this design change are:

1. UV transparency of the liquid phase would be maintained at a maximum.
2. There would be no pretreatment tanks, extra agitators or secondary compressors for vent gas from the UV/O<sub>3</sub> unit.
3. Periodic clean-out of sediment from the UV/O<sub>3</sub> unit would be eliminated.
4. Process control would be simplified because there would be no coordination problem between ozone quantities in the vent gas and the water feed rate. Analytical tests for manganese would be eliminated.
5. With no need for the ozone in the vent gas, the ozone feed rates and the reactor design could be adjusted for minimum ozone levels in the vent gas, which would correspond to maximum utilization of the only expensive raw material.

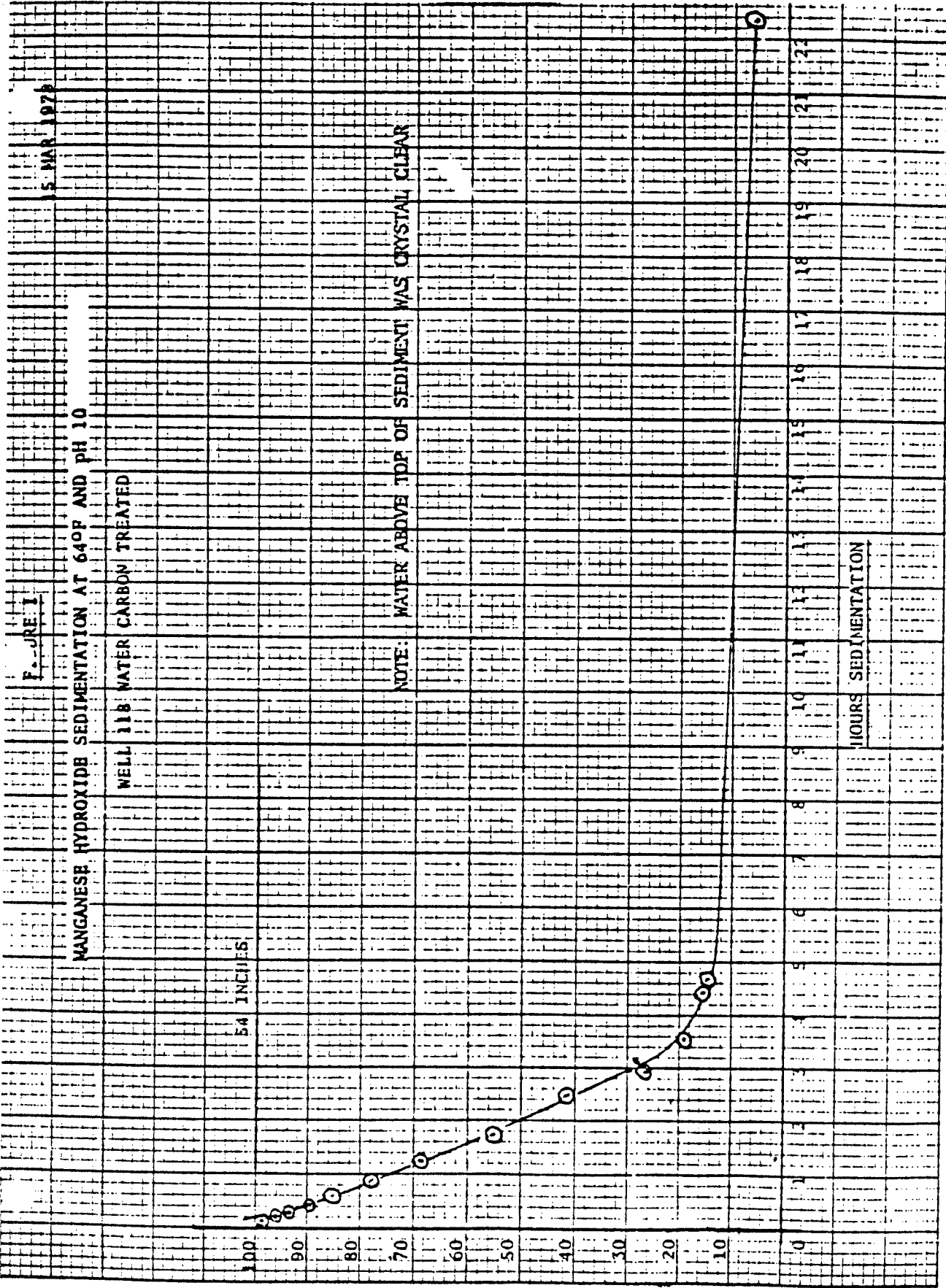
There are large capital, maintenance, and raw material savings to be realized from Items 2, 3 and 5. Costs for the ozone to react with 25ppm manganese plus 25ppm iron are shown by the dotted lines in Figure 3, for various water feed rates. Ozone cost is proportional to feed rate and is \$5.00 per day at 1000gph (1974 dollars), for 50% ozone utilization; much lower ozone utilization is probable, with correspondingly higher costs.

Future Work:

Recommend design and installation of a recirculating loop and filter for the UV/O<sub>3</sub> test unit due for installation at RMA. This modification should have priority over any oxidative pretreatment process because of its greater economy and simplicity.

# REFERENCES

1. Progress Report "Design of the Precipitation and Sedimentation Stage for Conditioning Water from Well 118 Prior to UV Ozonation", March 1978, RMA PD&ED.
2. Ralph B. Rozelle and Howard Swain, Jr., "Removal of Manganese from Mine Drainage by Ozone and Chlorine." Prepared for National Environmental Research Center, March 1975. PB-241-143 (NTIS)



PAGE 19  
TOP OF SEDIMENT (% OF DEPTH)

FIGURE 1

REDUCTION OF REACTOR SIZE BY STAGING

- A) RATE CONSTANT =  $5.4 \times 10^{-2}$   
 B) FLOW RATE = 50 gpm  
 C) CONTINUOUSLY FED STIRRED REACTOR

TOTAL REACTOR VOLUME (GALS.)

(NUMBER BY A CURVE  
IS THE NUMBER OF  
REACTION STAGES)

CONVERSION

PAGE 20

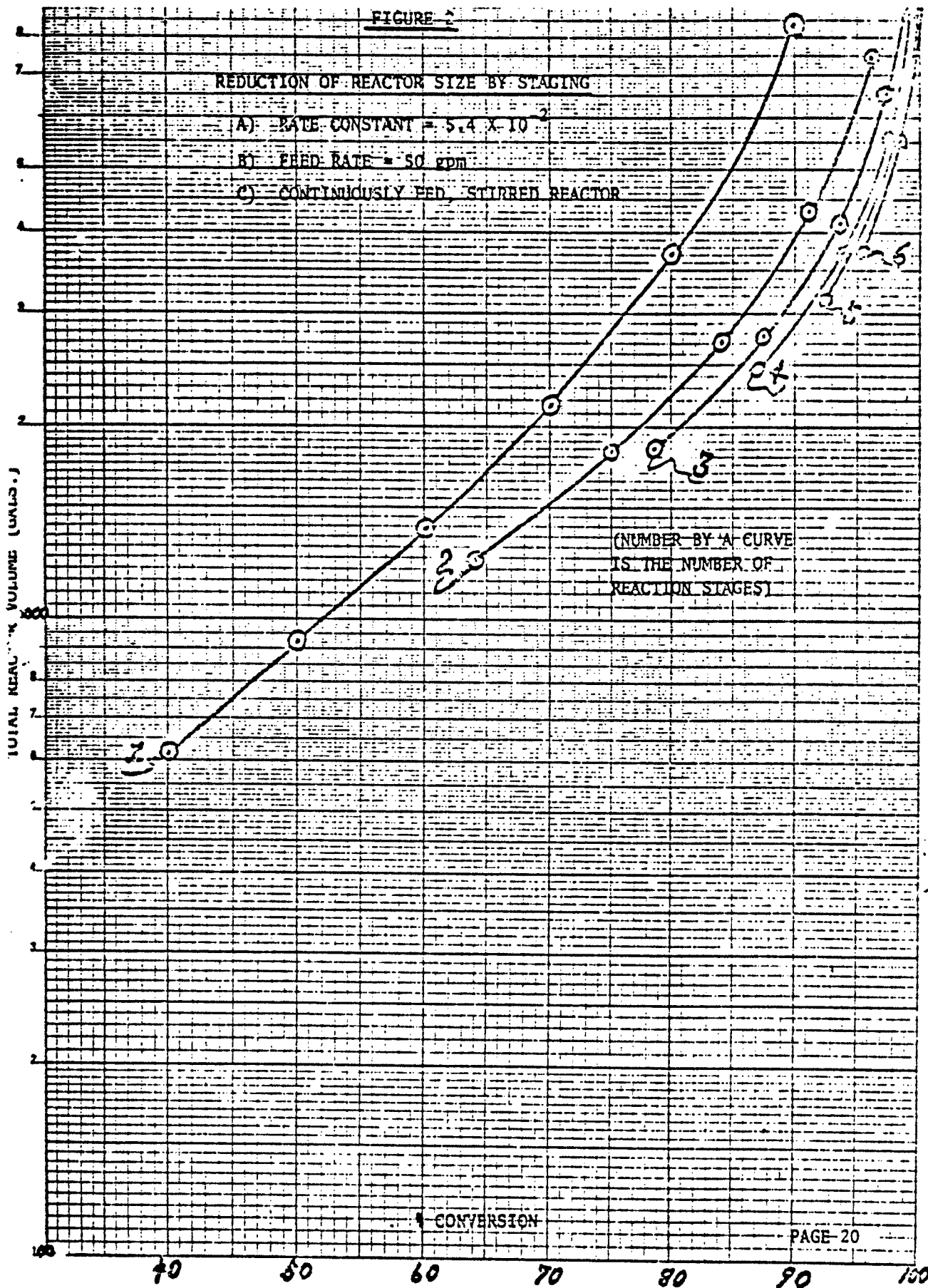


FIGURE 3

DATA FROM REF. 2. WITH RMA CASE FOR IRON AND MANGANESE PRECIPITATION SUPERIMPOSED AS DOTTED LINES. RMA CASE ASSUMES RECIRCULATION LOOP WITH FILTER IS ATTACHED TO  $UV/O_3$  UNIT.

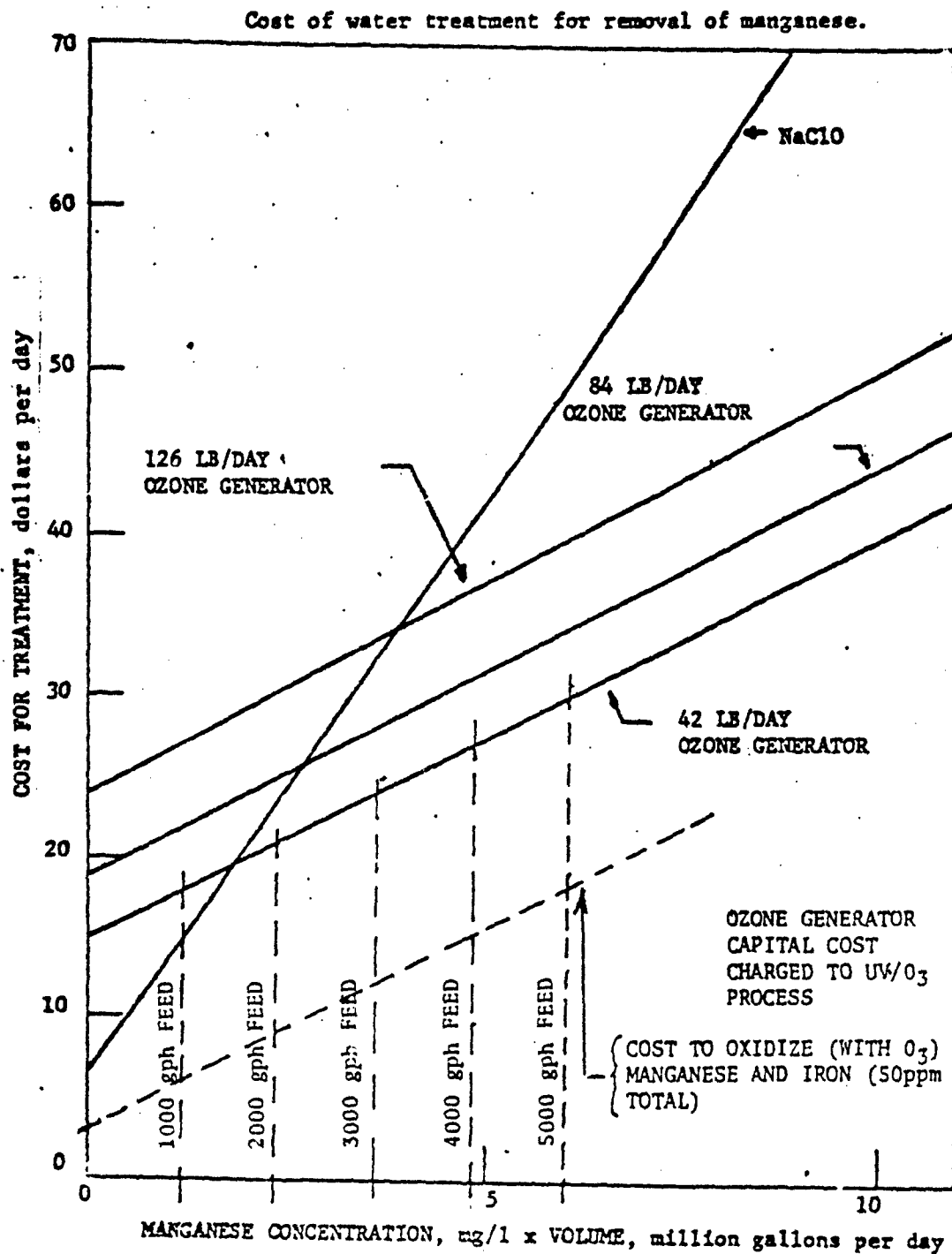




TABLE I

ESTIMATE OXYGEN SATURATION RATE IN 11.4 X 48 IN. TUBULAR REACTOR

OXYGEN CONCENTRATION\*

| <u>ELAPSED<br/>TIME<br/>(MIN)</u> | <u>DISSOLVED<br/>OXYGEN<br/>(PPM)</u> |
|-----------------------------------|---------------------------------------|
| 0                                 | 1.55                                  |
| 15                                | 7.34                                  |
| 45                                | 7.72                                  |
| 75                                | 7.78                                  |
| 105                               | 7.78                                  |
| 165                               | 7.78                                  |

\*Parameter: Air flow =  $4.8\text{ft}^3/\text{hr}$   
Temperature =  $62^\circ\text{F}$   
WATER SOURCE = TAP WATER

CONCLUSIONS: The dispersion system provides sufficient contact area for rapid transfer of oxygen into solution. This transfer rate will not be a limiting factor for oxidation reactions in solution, providing the total consumption is small.

At Denver's altitude, 7.8ppm is maximum oxygen concentration for a water solution at atmospheric pressure, using air as the oxygen source.

TABLE II

TEST TO ESTIMATE VOLATILES LOSS AND OXIDATION OF WELL 118 WATER  
"Aeration" of Same Sample with Nitrogen, Air, and Oxygen

| Elapsed<br>Time<br>Hours | DCPD<br>ppb | DITHIANE<br>ppb | SULFONES<br>ppb | DIMP<br>ppb | DMMP<br>ppm | COD<br>ppm | IRON<br>ppm | MANGANESE<br>ppm | NON-<br>FILTERABLE<br>SOLIDS<br>% | FILTERABLE<br>SOLIDS<br>% | TEMPERATURE<br>OF | FLOW<br>SCF/H |
|--------------------------|-------------|-----------------|-----------------|-------------|-------------|------------|-------------|------------------|-----------------------------------|---------------------------|-------------------|---------------|
| N <sub>2</sub> 0         | 1572        | 34              | 168             | 3320        | 300         | 490        | .41         | 29.2             | .01                               | 1.0                       | 56                | 5             |
| 2.9                      | 93          | 63              | 182             | 3506        | 300         | 580        | .61         | 15.2             | .03                               | 1.0                       | 67                | 5             |
| 6                        | <10         | 62              | 163             | 3332        | 300         | 640        | .12         | 7.7              | .03                               | 1.0                       | 67                | 5             |
| AIR                      |             |                 |                 |             |             |            |             |                  |                                   |                           |                   |               |
| .25                      | 33.4        | 57              | 140             | 3312        | 300         | 500        | .26         | 9.6              | .02                               | .9                        | 67                | 5             |
| .5                       | 35.4        | 59              | 140             | 3388        | "           | 480        | .15         | 8.1              | .02                               | "                         | "                 | "             |
| .75                      | 22.7        | 52              | 103             | 3508        | "           | 470        | .21         | 8.9              | .006                              | "                         | "                 | "             |
| 1                        | <10         | 47              | 116             | 3292        | "           | 430        | .11         | 8.2              | .004                              | "                         | "                 | "             |
| 1.5                      | 21.9        | 51              | 159             | 3247        | "           | 360        | .12         | 7.9              | .009                              | "                         | "                 | "             |
| 2                        | 13.8        | 65              | 186             | 3213        | "           | 420        | .16         | 7.7              | .005                              | "                         | "                 | "             |
| 3                        | 19.5        | 61              | 137             | 3101        | "           | 450        | .13         | 6.9              | .001                              | "                         | "                 | "             |
| 4                        | <10         | 76              | 127             | 3134        | "           | 480        | .15         | 6.3              | .004                              | "                         | "                 | "             |
| 21                       | <10         | 33              | 163             | 3117        | "           | 460        | .66         | 3.6              | .003                              | "                         | "                 | "             |
| OXYGEN                   |             |                 |                 |             |             |            |             |                  |                                   |                           |                   |               |
| 1                        | <10         | 75              | 133             | 3126        | "           | 460        | .27         | 3.4              | .002                              | "                         | "                 | "             |
| 2                        | <10         | 33              | 140             | 3200        | "           | 470        | .19         | 3.3              | .002                              | "                         | "                 | "             |
| 4                        | <10         | 31              | 115             | 3095        | "           | 470        | .14         | 3.0              | .002                              | "                         | "                 | "             |

CONCLUSION: DCPD is the only volatile lost; Manganese loss too slow for practical use.

TABLE III

TESTING MANGANESE OXIDATION BY AIR AFTER ORGANICS ADSORPTION  
ON CARBON TO REDUCE COD OF WELL 118 WATER

NOTE: Water passed through fresh carbon column was crystal clear and odorless.

| TIME<br>HRS. | TEMP.<br>OF | pH  | IRON<br>ppm | MN<br>ppm | COD<br>ppm | RATE K<br>Min <sup>-1</sup> |
|--------------|-------------|-----|-------------|-----------|------------|-----------------------------|
| 0            | 66          | 6.6 | 4.05        | 29.6      | 210        | --                          |
| .25          | 66          | 6.5 | 4.05        | 27.6      | 200        | --                          |
| .5           | 66          | 6.5 | "           | 29.2      | 200        | --                          |
| .75          | 66          | 6.6 | "           | 33.4      | 215        | --                          |
| 1            | 66          | 6.6 | "           | 29.7      | 250        | --                          |
| 1.5          | 66          | 6.7 | "           | "         | 220        | --                          |
| 2            | 66          | 6.7 | "           | 26.7      | 210        | --                          |
| 3            | 66          | 6.8 | "           | 23.9      | 200        | --                          |
| 4            | 66          | 6.8 | "           | 25.9      | 250        | $5.5 \times 10^{-4}$        |

CONCLUSION: Pretreatment with carbon did not change manganese oxidation rates; there is no improvement due to organics removal. COD results show that no organics oxidation is occurring. Evidently the lack of manganese oxidation is not due to organics interference.

NOTE : Rate constant calculation is not accurate; the carbon reduced COD from 580 to 210 ppm.

TABLE IV

TESTING MANGANESE OXIDATION WITH OXYGEN AFTER CARBON ADSORPTION  
TO REDUCE COD OF WELL 118 WATER

| TIME<br>HRS. | TEMP.<br>OF | pH  | IRON<br>ppm | MN<br>ppm | RATE K<br>Min <sup>-1</sup> | COD<br>ppm |
|--------------|-------------|-----|-------------|-----------|-----------------------------|------------|
| 0            | —           | 6.9 | <.05        | 29.6      |                             | 240        |
| .25          | 70          | 7.2 | "           | 29.6      |                             | 210        |
| .5           | 68          | 7.3 | "           | 26.8      |                             | 195        |
| .75          | 66          | 7.4 | "           | 29.2      |                             | 200        |
| 1            | "           | 7.5 | "           | 22.8      |                             | 190        |
| 1.5          | "           | 7.5 | "           | 19.3      | $4.8 \times 10^{-3}$        | 195        |
| 2            | "           | 7.4 | "           | 17.8      | $4.2 \times 10^{-3}$        | 205        |
| 3            | "           | 7.6 | "           | 17.2      | $3.0 \times 10^{-3}$        | 215        |
| 4            | "           | 7.6 | "           | 14.3      | $3.0 \times 10^{-3}$        | 210        |

- CONCLUSIONS: (1) Pure oxygen increases manganese oxidation rate by factor of about five ( $3 \times 10^{-3}/5.5 \times 10^{-4}$ )
- (2) No evidence of organics oxidation (COD is constant) by pure oxygen.

TABLE V

OXIDATION OF IRON AND MANGANESE WITH OZONE FROM AIR WITHOUT  
AUXILIARY AGITATION IN WELL 118 WATER

NOTES: A. Reactor is 11 3/8 by about 60 inches.  
B. Ozonizer operating at 60% power on air.  
C. Ambient temperature.  
D. Well 118 water filtered only through sand filter.

| TIME<br>HRS. | COD<br>ppm | IRON<br>ppm | RATE K<br>Min <sup>-1</sup> | MN<br>ppm | RATE K<br>Min <sup>-1</sup> |
|--------------|------------|-------------|-----------------------------|-----------|-----------------------------|
| 0            | 660        | 44.7        | —                           | 40.6      | --                          |
| 1.00         | 710        | 8.5         | $2.77 \times 10^{-2}$       | 36.4      | $1.8 \times 10^{-3}$        |
| 2.43         | 745        | 8.7         | $1.12 \times 10^{-2}$       | 23        | $3.9 \times 10^{-3}$        |
| 6.43         | 755        | 2.1         | $0.8 \times 10^{-2}$        | 1.6       | $8.4 \times 10^{-3}$        |
| 10.68        | 770        | 0.18        | $0.9 \times 10^{-2}$        | 4.05      | $10.5 \times 10^{-3}$       |

CONCLUSIONS: A. Ozone without UV has negligible effect on Well 118 COD in 10 hours at concentrations which will oxidize manganese.

TABLE VI

OXIDATION OF IRON AND MANGANESE IN WELL 118 WATER WITH OZONE  
FROM OXYGEN - SHOWING EFFECT OF AGITATION

NOTES: (A) Column is 4 inch diameter by about 60 inches.  
(B) Agitator is recirculation pump.  
(C) Ozonizer at 60% power on pure oxygen.

| NO AUXILIARY<br>AGITATION          | TIME<br>HRS. | IRON<br>ppm | RATE K<br>Min <sup>-1</sup> | MN<br>ppm | RATE K<br>Min <sup>-1</sup> | COD |     |
|------------------------------------|--------------|-------------|-----------------------------|-----------|-----------------------------|-----|-----|
|                                    | 0            | 25.4        | --                          | 27.6      | --                          | 550 |     |
|                                    | .25          | 3.67        | $1.3 \times 10^{-1}$        | 20.7      | $1.9 \times 10^{-2}$        | 570 |     |
|                                    | .5           | 4.93        | 7*                          | 19.0      | $1.2 \times 10^{-2}$        | 540 |     |
|                                    | 1            | 2.36        | 7*                          | 12.4      | $1.3 \times 10^{-2}$        | 595 |     |
| WITH AUXILIARY<br>AGITATION (PUMP) |              |             |                             |           |                             |     | pH  |
|                                    | 0            | 17.9        | --                          | 38        | --                          | --- | 7.3 |
|                                    | .033         | 1.6         | 1.2                         | 38        | --                          | --- | 7.9 |
|                                    | .083         | 1.9         | 7*                          | 36        | $1 \times 10^{-2}$          | --- | 8.1 |
|                                    | .167         | 1.7         | 7*                          | 32        | $1.7 \times 10^{-2}$        | --- | 8.2 |
|                                    | .250         | 1.0         | 7*                          | 17        | $5.3 \times 10^{-2}$        | --- | 8.0 |
|                                    | .500         | 0.5         | 7*                          | 2.1       | $5.6 \times 10^{-2}$        | --- | 8.1 |

\* - Indications of interference in iron analysis.

CONCLUSION: (A) Agitation improves ozonation rate by factor of four.  
(B) Ozone is about 18 times as fast as oxygen in manganese oxidation.  
(C) Estimated reactor size (gallons) if  $K=5.4 \times 10^{-2}$ .

$$V = \frac{G}{K} \left[ \frac{\% \text{ Conversion}}{100 - \% \text{ Conversion}} \right]$$

| Conversion | 10gpm   | 25gpm   | 50gpm   | 2gpm   |
|------------|---------|---------|---------|--------|
| 80%        | 740     | 1851    | 3703    | 148    |
| 90%        | 1667    | 4167    | 8333    | 333    |
| 95%        | 3518    | 8796    | 17,600  | 700    |
| 99%        | 18,300  | 45,830  | 91,600  | 3666   |
| 99.9%      | 105,000 | 462,500 | 925,000 | 37,000 |

(D) Would have to multiply ozonation rate by 100 or so to meet level of .05 ppm manganese at a reasonable rate of flow in a practical size vessel.

TABLE VII

EXERCISE ILLUSTRATING THE REDUCTION IN REACTOR VOLUME OBTAINABLE WHEN A SINGLE, CONTINUOUSLY FED, STIRRED REACTOR IS REPLACED BY A SERIES OF N SIMILAR (BUT SMALLER) REACTORS. ASSUMED FEED RATE OF 50gpm AND  $K = 5.4 \times 10^{-2} \text{ min}^{-1}$ . VALUES SHOWN ARE FROM EQUATION A/ BELOW:

| STAGE<br>NO<br>(N)                         | FOR EACH STAGE OF THE SERIES<br>CONVERSION % ASSUMED CONSTANT AT: |       |        |        |                     |
|--------------------------------------------|-------------------------------------------------------------------|-------|--------|--------|---------------------|
|                                            | 40%                                                               | 50%   | 60%    | 70%    | 80%                 |
| 1.1 REACTOR VOLUME (GALS) <u>A/</u>        | 617                                                               | 925   | 1389   | 2160   | 3703                |
| .2 ACCUMULATIVE CONV. (%) <u>B/</u>        | 40                                                                | 50    | 60     | 70     | 80                  |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 617                                                               | 925   | 1389   | 2160   | 3703                |
| .4 (1.1/1.3) X 100 (% OF 1 STAGE)          | 100                                                               | 100   | 100    | 100    | 100                 |
| 2.1 REACTOR VOLUME (2 STAGES)              | 1234                                                              | 1850  | 2778   | 4320   | 7406                |
| .2 ACCUMULATIVE CONV. -2 STAGES <u>B/</u>  | 64                                                                | 75    | 84     | 91     | 96                  |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 1646                                                              | 2777  | 4961   | 9362   | 22222               |
| .4 (2.1/2.3) X 100 (% OF 1 STAGE)          | 75                                                                | 67    | 57     | 46     | 33                  |
| 3.1 REACTOR VOLUME (3 STAGES)              | 1851                                                              | 2775  | 4167   | 6480   | 11109               |
| .2 ACCUMULATIVE CONV. (3 STAGES) <u>B/</u> | 78.4                                                              | 87.5  | 93.6   | 97.3   | 99.2                |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 3360                                                              | 6481  | 13541  | 33367  | 114814              |
| .4 (3.1/3.3) X 100 (% OF 1 STAGE)          | 55                                                                | 43    | 31     | 19     | 10                  |
| 4.1 REACTOR VOLUME (4 STAGES)              | 2468                                                              | 3700  | 5556   | 8640   | 14812               |
| .2 ACCUMULATIVE CONV. (4 STAGES) <u>B/</u> | 87.0                                                              | 93.4  | 97.4   | 99.2   | 99.8                |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 6196                                                              | 13103 | 34686  | 114814 | 462037              |
| .4 (4.1/4.3) X 100 (% OF 1 STAGE)          | 40                                                                | 28    | 16     | 8      | 3                   |
| 5.1 REACTOR VOLUME (5 STAGES)              | 3085                                                              | 4625  | 6945   | 10800  | 18515               |
| .2 ACCUMULATIVE CONV. (5 STAGES) <u>B/</u> | 92.2                                                              | 96.9  | 99.0   | 99.8   | 99.97               |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 10944                                                             | 28942 | 91666  | 462037 | 3.1X10 <sup>6</sup> |
| .4 (5.1/5.3) X 100 (% OF 1 STAGE)          | 28                                                                | 16    | 8      | 2      | 1                   |
| 6.1 REACTOR VOLUME (6 STAGES)              | 3702                                                              | 5550  | 8334   | 12960  | 22218               |
| .2 ACCUMULATIVE CONV. (6 STAGES) <u>B/</u> | 95.3                                                              | 98.4  | 99.6   | 99.9   | 99.99               |
| .3 VOL. ONE STAGE (GALS) <u>C/</u>         | 18779                                                             | 56944 | 230555 | 925000 | 9.3X10 <sup>6</sup> |
| .4 (6.1/6.3) X 100 (% OF 1 STAGE)          | 20                                                                | 10    | 4      | 1      | .2                  |

A/ -  $V = \frac{G}{K} \left[ \frac{\% \text{ CONV.}}{100 - \% \text{ CONV.}} \right]$  where  $G = 50\text{gpm}$ ;  $K = 5.4 \times 10^{-2}$ ; V is the reactor volume for obtaining the given conversion in one stage.

B/ - Reactor volume is the same for each stage at a fixed conversion level; each stage converts a fixed % of the incoming raw material.

C/ - Is the single-stage volume necessary to reach the accumulative conversion obtained by the N stages (Equation under A).