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January 1982

Catalytic Oxidation of Sulfur Dioxide in Wastewater

Ernest J. Upton

V. Dean Adams

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CATALYTIC OXIDATION OF SULFUR

DIOXIDE IN WASTEWATER

by

Ernest J. Upton V. Dean Adams

Report to

International Environmental, Inc. Salt Lake City, Utah

Submitted by

Utah Water Research Laboratory Utah State University Logan, Utah 84322 in 19

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ACKNOWLEDGMENTS

This publication represents the final report of a project evaluating the catalytic oxidation of sulfur dioxide in wastewater which was supported by funds provided by International Environmental, Inc. of Salt Lake City, Utah.

The authors express gratitude to all who contributed to the completion of this study. A sincere thanks is also extended to the Utah Water Research Laboratory for providing laboratory equipment and facilities necessary to complete this study and to the capable editorial and secretarial staff for their assistance in preparation and publication of this report.

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ABSTRACT

Sulfur dioxide has been shown to be an effective wastewater disinfectant. The aqueous sulfur dioxide creates an oxygen demand in the effluent which must be removed prior to discharge. Oxidation to sulfate is one means of accomplishing this task.

Experiments were carried out to determine the effectiveness of transition metals and activated carbon as catalysts for the oxidation of S+IV species in wastewater. Both the metals and carbon are known catalysts, but what inhibitory effect the wastewater might have was unknown. Effectiveness was defined as a combination of catalyst life, effluent quality, and cost.

Transition metals were eliminated as potential catalysts due to the high metal concentrations found in the effluent. The acidic nature of 500 mg/1 SO₂ dissolved in wastewater (pH 2.5) would dissolve the metals or cause them to desorb from a carbon base.

Using downf1ow contactors, activated carbon was shown to catalyze the reaction as long as sufficient oxygen was available. At a loading rate of 5.5 g carbon/1 and a hydraulic loading of 38 $\text{M}^3/\text{M}^2\cdot$ day, 24 hour runs were accomplished without SO_2 breakthrough (less than 4 mg/1). Longer runs resulted in gradual breakthrough (40 mg SO $_2/1$ after 96 hours). The cause of the failure was assumed to be the self-poisoning of the catalyst by sulfuric acid (the product of $so₂$ oxidation) and/or the reduced solubility of oxygen in the sulfuric acid solution. Carbon regeneration, as a catalyst, was accomplished by backwashing the column with tap water. The cost of sulfur dioxide disinfection ranged from \$0.23-\$0.73/1000 gallons treated. In general, this process was much more costly than other disinfection systems.

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INTRODUCTION

The use of chlorine as a wastewater disinfectant is receiving worldwide attention with respect to its potential adverse health effects. This is partially due to the formation of chlorinated organics which may be carcinogenic. Sulfur dioxide has been shown to be an effective disinfectant (Reynolds and Adams 1979). Sulfur dioxide is a strong reducing agent and when dissolved in water forms sulfite, bisulfite, or sulfurous acid, depending on the pH of the solution. The majority of the sulfur species remains essentially unchanged during and following the disinfection process. Sulfite and bisulfite ions are quite reactive and create an oxygen demand. This oxygen demand must be removed if wastewater discharge requirements are to be met. Oxidation of the sulfite and bisulfite ions to sulfate, catalyzed by transition metals or activated carbon, is one means of removing the oxygen demand.

There are other means of controlling sulfite. Watkins (1977) in his summary of methods for controlling sulfur compounds lists biological, chemical precipitation, electrodialysis, ion exchange, and reverse osmosis. Hesketh and Potokar (1977) found (by bubbling 1100 ppm $S0₂$ gas through fly ash or carbon slurries) that fly ash from coal burning operations had a sorptive capacity three times greater than activated carbon. Neither the type of carbon nor its catalytic oxidative capacity was compared, however.

Strong oxidants have also been investigated. Penkett et al. (1979) studied the effects of ozone and hydrogen peroxide on the oxidation of aqueous sulfur dioxide to sulfate.

Most of these latter means of controlling sulfite are considered too costly for large scale operations such as sewage treatment facilities using sulfur dioxide for disinfection. Therefore, the focus of this research shall be the catalytic oxidation of aqueous sulfur dioxide by transition metals and/or activated carbon.

OBJECTIVES

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The main objective of this research is the development of an efficient means of removing the oxygen demand created in wastewater following disinfection by sulfur dioxide. Specific objectives include:

- 1. Determination of an efficient catalyst for the oxidation of sulfite or bisulfite in wastewater.
- 2. Development of design parameters for use of the catalyst as a means of removing sulfite from wastewater.
- 3. Development of costs associated with use of the catalyst in sulfur dioxide-wastewater disinfection systems.

LITERATURE REVIEW

The oxidation of aqueous sulfur dioxide has been the subject of a great deal of research. This reaction does not occur at a measurable rate at low pH (0-3) without a catalyst present (EPA 1981), Thus most of this research has dealt with obtaining kinetic data in the presence of various catalysts.

Metal Catalysts

Fuller and Crist (1941) studied the effects of copper and pH on the rate of oxidation of sulfite in distilled water using pure oxygen. They found that copper ion concentrations greater than 10^{-9} M greatly increased the rate of oxidation. Lowering the pH from 8.2 to 3.2 decreased the rate of oxidation. Fuller and Crist accounted for this pH phenomenon by assuming the rate of oxidation is dependent on the sulfite ion concentration and the square root of the hydrogen ion concentration.

Other metals such as cobalt and manganese also catalyze the oxidation of aqueous sulfur dioxide. Coughanowr and Krause (1965) used manganous sulfate $(0-6.6 \times 10^{-4} \text{ M m}^2)$ as a catalyst and determined a reaction rate proportional to the square of the catalyst concentration. Their SO_2 concentration was approximately 1.7 x 10^{-3} M in distilled water saturated with oxygen. Cobaltous sulfate $(10^{-7} 3 \times 10^{-6}$ M Co²⁺) as a catalyst was shown by Chen and Barron (1972) and Bengtsson and Bjeiles (1975) to affect the reaction rate (of 9.4 \times 10⁻³ M SO₂ in distilled water) by the square root of the catalyst concentration.

The previous results were obtained under solution pH greater than 6.0. At low pH $(0-3)$ the EPA (1981) found cobalt $(2.5 \times 10^{-5} \text{ M})$ to be an ineffective catalyst; the catalyzed reaction was second order in manganese $(2 \times 10^{-5} - 2.5 \times 10^{-4})$.

Tiwari et al. (1979), 1n studying the oxidation of ferrous sulfate under acidic conditions found that SO_2 would catalyze the reaction. This indicates that iron is another metal capable of increasing the rate of oxidation of sulfur dioxide. The EPA (1981) reported that iron $(2.0 \times 10^{-5}$ M Fe³⁺) did catalyze the reaction under acidic conditions and that the reaction was first order in iron.

Brimblecombe and Spedding (1974) found in their work that the reaction order of the oxidation of sulfite was dependent on the pH of the solution. A 0.1 M ammonium sulfate solution containing 10^{-5} M of S+IV in the presence of 10^{-6} M Fe(III) was used to simulate aqueous atmospheric aerosols. They were able to show, using steady-state principles, that at low sulfite ion concentrations (low pH conditions) the reaction is first order with respect to sulfite ion concentrations. At higher sulfite ion concentrations (higher pH conditions) the reaction appears to be second order. Thus it can be concluded from this work that the rate of oxidation of sulfite in the presence of a metal catalyst is pH dependent.

Activated Carbon

The oxidation of S+IV species is catalyzed by activated carbon. Air pollution research has provided a great deal of information in this area.

Siedlewski (1965) and Novakov and Chang (1975) determined that sulfur dioxide in air would chemisorb to the surface of the activated carbon at points where free carbon radicals exist. The quantity of sulfur dioxide oxidized is a function of the number of these active sites on the carbon, and not the quantity of sulfur dioxide or oxygen present.

The adsorptive capacity and catalytic activity of activated carbon appear to be a function of the number of free radical sites on the carbon. Seaburn and Engel (1973) bubbled SO₂ gas through slurries of activated carbon (using several different commercial brands of activated carbon) and determined that the number of these free radical sites was dependent on the source material for the carbon.

Komiyama and Smith (1975) found that the rate of oxidation of sulfur dioxide in slurries of activated carbon was first order with respect to oxygen concentration and zero order with respect to sulfur dioxide. They concluded that the controlling step of the oxidation mechanism is the adsorption of oxygen on the active sites of the carbon.

It is fairly well established that surface carbon-oxygen complexes are responsible for activated carbon's catalytic ability.

The reaction mechanism between sulfite and activated carbon is more than a simple reaction with surface adsorbed oxygen, however (Eatough et al. 1979). Free radical carbon sites are probably involved in the complexation of sulfite and carbon, resulting in the formation of sulfate. Eatough et al. concluded that oxidative regeneration of these active sites is the rate limiting step in the oxidation of sulfite on activated carbon.

The rate of the oxidation reaction has been found to be independent of the pH at values less than 7.6. Above a pH of 7.6 the rate of reaction drops to zero thus, indicating a poisoning of the carbon (Chang et al. 1976-77; Brodzinsky et al. 1980). Eatough et al. (1979) proposed that bisulfite was the reacting species. However, Brodzinsky et al. concluded that it is the carbon's active site, affected by pH, that causes the change in rate of oxidation.

Although some confusion exists as to the mechanism, it is generally agreed that activated carbon is an effective catalyst in the oxidation of sulfur dioxide.

EXPERIMENTAL APPARATUS AND PROCEDURES

A review of the pertinent literature concerning catalytic oxidation of sulfur dioxide showed that the primary experimental procedure used involved jar tests to obtain kinetic data (Komiyama and Smith 1975; Chang et al. 1976-77; Brodzinsky et al. 1980). To obtain data necessary to meet the objectives of this study, upflow and downward contactors, in addition to jar tests, were utilized.

Catalysts

Filtrasorb 400, manufactured by Calgon Corporation, was the activated carbon used in the jar tests. Filtrasorb 300 was used in all column experiments. Specifications given by the manufacturer have been included in Appendix A.

The wide range of particle sizes provided in the Filtrasorb 300 was found to be unacceptable for use in the column experiments because the finer particles would quickly flush out of the column and thus be unavailable as a catalyst. It was determined that the carbon retained on a 24 mesh sieve would function the best in the column experiments. The carbon was placed in the 24 mesh sieve and washed with chlorine free tap water to remove the fines. If used in conjunction with a metal catalyst, the carbon was then dried for 24 hours at 103°C. If used alone, the carbon was air dried overnight for use the following day.

Metal catalysts were used in conjunction with the activated carbon by adsorbing the desired metal onto the carbon. A metallic ion solution (FeC13 or MnC12, for example) was made based on adsorbing

2 or 6 mg metal ion per g carbon. The carbon was added to the solution and shaken for one hour. The liquid was separated from the carbon and tested for metal ion content to determine the actual amount of metal ion adsorbed. The carbon was rinsed with tap water to remove excess metal ion solution and then considered ready for use in the column.

Also, metal catalysts alone were used in the downflow contactors. They took the form of 3.2 mm inert pellets covered with metal oxides. Catalysts used were manganese oxide (19 percent) on alumina, ferric oxide (20 percent) on alumina, nickel-cobalt-iron oxide (3 percent each) on alumina, and vanadium oxide (10 percent) on alumina-silica (all manufactured by Alfa Products), The catalysts were rinsed with tap water prior to being placed in the column to remove excess powder created during shipping.

Plain, 3/8-inch iron nuts were used as a catalyst in jar tests. The nuts were soaked in 6N HCl for several hours then rinsed with tap water prior to immediate use.

Sulfur Dioxide and Sewage Source

The source of sulfur dioxide for all experiments was reagent grade sulfurous acid produced by J. T. Baker Chemical Co. or Fisher Scientific Co. Sufficient sulfurous acid was added to the sewage to maintain a concentration of 500 mg/l as SO_2 . This is referred to as the "feed solution."

Sewage used for all experiments was secondary clarifier effluent obtained from the City of Hyrum's oxidation ditch wastewater treatment plant. Typical characteristics are shown in Table 1.

Parameter	Value
BOD ₅	$15 - 20$ mg/1
DO.	$5.5 - 6.0$
\sim pH	$7.5 - 8.0$
Alkalinity	270 mg/l as $CaCO3$

Table 1. City of Hyrum secondary clarifier effluent characteristics.

Analytical Procedures

Sulfite concentrations were measured using the oxidation-reduction titration procedure described on pp. 451-452 of Standard Methods (APHA 1980). Sulfate concentrations were measured using the turbidimetric methods described on pp. 439-440 of Standard Methods (APHA 1980). A Bausch-Lomb Spec 70 set at 420 nm with a 5 cm light path was used to measure light absorbance.

Dissolved oxygen was measured using a YSI meter #54A and a YSI probe #5740. As effects of long term (i.e., hours) exposure to S=IV are unknown, the electrode membrane was changed daily (Reynolds and Adams 1979). The meter was calibrated by aerating tap water for 30 minutes to achieve saturation; a chart was used to calculate the saturation of oxygen based on temperature and altitude. The pH was measured using a Beckman Zeromatic II meter and a combination electrode.

Metal analysis was by atomic absorption using a Varian Model AA-6. Cobalt, iron, manganese, and nickel concentrations were determined using the direct aspiration method and vanadium was determined by the graphite furnace technique (EPA 1979; APHA 1980).

Experimental Procedures

Jar tests

Initial experimentation involved the determination of the ability of granular activated carbon to either adsorb or oxidize sulfite in wastewater. Carbon adsorption isotherms were developed for this purpose. Carbon amounts from 0 to 15 g were added to six 500 ml Erlenmeyer flasks; 250 ml secondary sewage from the Hyrum treatment plant containing 500 mg/l sulfur dioxide (SO_2) was then added to each flask. The flasks were stoppered with aluminum foil covered rubber stoppers and mixed for 2 hours at 150 rpm (see Figure 1). The samples were then filtered using a Millipore filter and analyzed for sulfite $(SO_3⁼)$, sulfate (SO_4^*) , pH, and dissolved oxygen (DO). Isotherms were also developed to determine the effect of various metals adsorbed to the carbon. Metals used were iron and manganese. Adsorption of the metal to the carbon was discussed earlier.

Jar tests involving raw iron were conducted by placing iron nuts in the bottom of a 4000 ml beaker containing the sewage and $S0₂$. The solution was aerated at 500 ℓ /hr to assure that dissolved oxygen was not limiting. Iron, SO_2 , dissolved oxygen, and pH were measured at one minute intervals.

Upflow contactor

The upflow contactor apparatus consisted of a 5 gallon feed tank, a variable speed centrifugal pump (Micropump, Inc,), a flowmeter (Laboratory Supplies, Inc.) calibrated for 0.6-5 gph (38-315 ml/min), and a 5 em diameter glass column. The apparatus is shown schematically in Figure 2.

Figure 1. Jar test apparatus.

Figure 2. Bench scale upflow contactor.

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Three upflow columns were run, each with a different media: activated carbon with either iron, cobalt, or manganese adsorbed to it. Columns were operated at 100 ml/min for one hour. Samples were collected at five minute intervals and analyzed for DO, pH, SO_3^{\pm} , SO_4^{\pm} , and the particular metal adsorbed to the carbon.

Downflow contactor

Initial downflow contactor runs utilized the same equipment as the upflow contactor. The only exception was insertion of a glass fritted gas dispersion tube in the side of the column to allow for aeration (see Figures 3, 4, and 5). Equipment changes made during the course of these experiments include replacement of the Micropump with a variable speed peristaltic pump (Masterflex Model 7016) and replacement of the flowmeter (Gilmont Compact Flowmeter #13, 2-300 ml/min). These changes were made to improve equipment performance.

Column runs using the metal oxides as the medium lasted 3 hours. A liquid flow rate of 50 ml/min and an air flow rate of 500 ℓ /hr were used. Medium depth was 25 cm.

Column runs using activated carbon or activated carbon plus metals initially lasted 6 hours, but were later extended to 24 hours. Liquid flow for all runs was 50 ml/min; air flow varied, 0 or 500 ℓ/nr . Medium depth was 25 cm.

Evidence of short circuiting along the glass wall of the column prompted replacement of the 5 cm column with an 8.5 cm diameter column (see Figure 6). The interior surface of the column was coated with activated carbon to further eliminate short circuiting. The adhesive used was silicon (GE 8CSlOOO).

Figure 3. Bench scale downflow contactor.

Figure 4. 5 cm downflow contactor.

Figure **6.** 8.5 em downflow eontactor.

All column runs using the larger column utilized activated carbon as a catalyst. Other column parameters varied as shown in Table **2.** Prior to all column runs, chlorine free tap water was poured down the column to saturate the carbon.

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RESULTS AND DISCUSSION

Sulfur dioxide has been shown to be an effective wastewater disinfectant (Reynolds and Adams 1979). Disinfection was found to be a function of three parameters, $S0₂$ concentration, time, and pH value. It was shown that 160 mg/1 SO_2 and a pH of 2.5 is the optimal combination of these two parameters at a 30 minute detention time. Using these values, the total coliform count can be reduced to less than 200 organisms/100 ml and fecal coliform counts to less than 20 organisms/lOa mI. To obtain a pH value of 2.5 in high alkalinity wastewater (250-300 mg/l as CaCO3) a mineral acid must be added in addition to the 160 mg/1 SO_2 , or 500 mg/1 SO_2 must be added to the wastewater. This research has been based on the latter case.

Sulfur dioxide dissolved in water will form either sulfite (SO_3^m) , bisulfite (HSO_3^-) or sulfurous acid (H_2SO_3) depending on the pH of the solution. This is depicted graphically in Figure 7 (EPA 1979). It should be noted that Figure 7 is not quantitative in that all activity coefficients are assumed to be unity. It does show a qualitative relationship between aqueous SO₂ species.

As noted, with a SO₂ concentration of 500 mg/l, the pH of the secondary sewage used in these experiments is approximately 2.6 (depending on the alkalinity of the sewage). Thus the dominant species in solution will be HSO_3^- . Oxidation of HSO_3^- leads to the formation of sulfate plus a proton:

$$
HSO_3^- + 1/2 O_2 + H^+ + SO_4^-
$$
 (1)

Schmidt (1972) noted that the formation of dithionate is increased at low pH:

$$
2HSO_3 = S_2O_5^- + H_2O
$$
 (2)

$$
S_2O_5^{\pi} + H_2O \to S_2O_6^{\pi} + 2H^+ + 2e^{\pi}
$$
 (3)

Dithionate is a very stable ion and will not undergo oxidation or reduction very easily. The oxidation state of dithionate (S+V) is not the same as sulfite (S+IV) or sulfate (S+VI). Thus dithionate is not detected by the analytical procedures used to measure sulfite or sulfate. Later discussion of the sulfur mass balance will return to this point.

All sulfur specie concentrations in the following discussion are reported in mg/1 as SO_2 .

Jar Tests

The jar tests clearly indicate the catalytic abilities of activated carbon. The results were plotted as carbon adsorption isotherms. A favorable isotherm is one with an initial steep use at the low carbon masses. The carbon isotherm shown in Figure 8 would be considered unfavorable. The concentration of carbon necessary to completely remove the $SO₂$ was found to be 40 g/1. The pH increased from an initial 2.6 to 3.6. At higher carbon concentrations, the pH continued to increase, indicating that the activated carbon was removing the products of bisulfite oxidation from solution.

The jar tests involving activated carbon with adsorbed metals produced more favorable isotherms (Figure 9). The metals reduced the carbon concentration necessary for complete removal of $SO₂$ by

Figure 8. SO_2 removal-jar test results.

Figure 9. SO_2 removal-jar test results.
half, to 20 g/l. However, the gain in reduced carbon concentration was offset by desorption of the metals from the carbon. For example, the solution containing 50 $g/1$ of carbon with 6 mg/g of iron adsorbed measured 51 mg/l iron at the end of the test. The reason for desorption of the metals is assumed to be the low pH (2.8) of the solution.

Removal of the bisulfite oxidation products by the carbon was again observed in these experiments. This assumption is proven by considering the mass balance of sulfur species. As shown in Table 3, the effluent sulfur species decrease with increasing carbon concentrations. With no carbon, the data show a loss of 107 mg/1 SO_2 after two hours of shaking. Approximately one-third of this loss is due to oxidation to SO_4 ⁼; the remainder is assumed to have gone off as gaseous $50₂$. As discussed earlier, dithionate may have been formed and would account for some of the missing sulfur.

The results of the carbon jar tests indicate that activated carbon is not very efficient (requiring 40 g/1) at removing SO_2 from wastewater. However, insufficient dissolved oxygen appeared to limit the oxidation of the $50₂$ and therefore biased the results. Thus the impetus for column experiments was to further define the catalytic capabilities of carbon.

Jar tests involving raw iron as a catalyst also showed the adverse effects of the acidic solution. As shown in Figure 10, at an iron concentration of 20 mg/1 the rate of $S0₂$ and DO reduction is rapid and constant. Further increases in the iron concentration do not affect the rate of reaction. As the reaction rate did not increase until 20 mg/1 of iron was present it can be concluded that iron, as a catalyst, must be dissolved in solution. The catalytic effect is probably not a sur-

Carbon Conc. g/1	Final SO ₂ mg/1	Final SO_4 ⁼ as $S02$	Total SO ₂ mg/1	
Initial Solution	500	39	539	
0	364	68	432	
10	32	448	480	
20	6	382	388	
30	$\mathbf 0$	371	371	
40	0	278	278	
50	0	240	240	

Table 3. Typical sulfur mass balance.

Note: Data from Appendix B, Table B-7. Figure 10. Oxidation of SO₂ using raw iron.

face phenomenon on the iron. Although a good catalyst, the use of raw iron does not appear feasible due to the high concentration $(20 \text{ mg}/1)$ of iron in the effluent.

Up flow Contactors

Three upflow columns were operated using either iron, manganese, or cobalt adsorbed to activated carbon. The results of the carbon and manganese column are shown in Table 4. The results are very similar to the jar tests, and show activated carbon with metals to be a very efficient catalyst as long as a sufficient stoichiometric amount of oxygen is present to complete the oxidation. The data also show that the acidic nature of the feed solution causes the metal to desorb from the carbon. As with the jar tests, insufficient oxygen did not allow for long term analysis of the catalytic capabilities of activated carbon.

Time (min)	DO.	pH	SO ₂ mg/1	SO_4 ⁼ as $SO2$	Mn^{++} mg/1	
Initial	6.8	2.4	548	49	≤ 4	
5	2.2	5.0	0	388	178	
10	2.2	4.1	0	403	182	
15	1.7	3.2	$\mathbf 0$	388	156	
20	0.2	2.5	$\overline{0}$	352	105	
25	0	2.4	32	395	91	
30	$\mathbf 0$	2.4	48	395	89	
35	$\overline{0}$	2.4	136	344	55	
40	$\overline{0}$	2.4	168	358	49	

Table 4. Typical upflow column data using activated carbon + Mn++ medimn.

Downflow Contactors

Downflow columns using eight different media were operated for 3-6 hour periods. The purpose of these runs was to make a preliminary assessment of the oxidative capacity of the various media. The results are summarized in Table 5 (raw data are included in Appendix B, Table $B-2$ through $B-5$).

None of the alumina base metallic media completely oxidized the SO₂ for any length of time. As excess air (500 ℓ /hr) was being pumped into the column, the extremely large effluent SO₂ concentration should not have been caused by depleted oxygen levels. Insufficient detention time could have caused the breakthrough however. Increasing detention time was not attempted due to the primary reason for dismissing use of these media as catalysts: high metal concentrations in the effluent. Figure 11 shows the manganese catalyst before and after the column run. The removal of the manganese from the base alumina is clearly evident, again, due to the acidic nature of the feed solution.

Study of activated carbon and activated carbon plus metals continued with 24 hour runs. The purpose was to determine the maximum $S0₂$ breakthrough (if one existed) and the extent of metal desorption from the carbon. Metals used were cobalt, iron and manganese. Excessive air (500 ℓ /hr) was again used to prevent depleted oxygen levels from affecting catalyst evaluation.

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S02 breakthrough occurred within 2 hours in all columns except the carbon-manganese column which lasted 5 hours (see Appendix B, Tables B-8 through B-16). On the basis of a single run, the carbonmanganese column had a maximum breakthrough of 28 mg/1; 68 mg/1 for the

Table 5. Preliminary assessment of oxidation catalysts.

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Column Conditions: 
Feed Rate = 50 ml/min.
Medium Depth = 25 cm
Feed Soln. pH = 2.5 - 2.9Air Flow = 7.2-9.5 \ell/min.
Run Time = 3 hrs.
```


*Oxidative Capacity (Effluent SO_2 Concentration): Good ≤ 50 mg $SO_2/1$; Fair \langle 100 mg $\frac{100}{2}$ /1; $\frac{100}{2}$ /1; Poor $>$ 100 mg $\frac{100}{2}$ /1 $\frac{100}{2}$ Effluent DO: Good ≥ 2 mg/l; Poor ≤ 2 mg/l Effluent pH: Good ≥ 6.5 ; Poor $\lt 6.5$ Effluent Metals: Good \leq 1 mg/1; Fair \leq 5 mg/1; Poor > 5 mg/1

Figure 11. Manganese oxide on alumina before and after column **run.**

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carbon-cobalt column (see Figure 12). Both columns did reasonably well based on metal desorption. The maximum cobalt concentration in the effluent was 5.8 mg/l; the values dropped to less than 1 mg/l after 3 hours. The manganese effluent concentration peaked at $6.1 \text{ mg}/1$ and dropped to less than 1 mg/l after 3 hours.

Of three runs using carbon-iron medium two had similar peak $SO₂$ effluent values of 16 and 38 mg/l. The third run exhibited a much higher breakthrough however (see Figure 13). Iron desorption was higher than the other metals. Concentrations of $60 \text{ mg}/1$ were measured at the beginning of the runs. Values decreased to approximately 1 mg/l after 24 hours.

The results of three runs using activated carbon medium are shown in Figure 14. As shown, the results were extremely variable. Five additional runs were completed, with zero air flow, in an attempt to replicate results (Figure 15 and Appendix B, Tables B-18 through B-22). Again, results were variable. As all column parameters were equal for these runs, it was determined that the cause of the variable results was short-circuiting down the glass column walls. Increasing the column diameter from 5 cm to 8.5 cm increased the carbon volume to glass wall area ratio by 70 percent. It also produced much more consistent results (Figure 16 and Appendix B, Tables B-22 through B-26).

At this point it was decided to eliminate the carbon plus metal catalyst from further study and concentrate on activated carbon. This decision was based on the desorption of the metals into the influent. The acidic nature of the feed solution would not allow the activated carbon to retain the metal ions.

Figure 12. SO_2 breakthrough using activated carbon and metals medium.

Note: 8/31 (i.e.) refers to date of experiment

Figure 13. SO_2 breakthrough using activated carbon + iron medium.

Figure 14. SO_2 breakthrough using activated carbon medium.

Figure 15. Variation in SO_2 breakthrough for 5-24 hour runs (5 cm column).

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Figure 16. Variation in SO_2 breakthrough for 5-24 hour runs (8.5 cm column).

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Starting with the 8.5 cm column, other column parameters were varied while the medium was held constant as shown in Table 2. Figure 17 (Table $B-24$) shows the effects of zero air flow in the column. As before, insufficient oxygen caused column failure indicated by zero dissolved oxygen measurements. The increasing oxygen levels along with increasing SO_2 is indicative of catalyst poisoning. As the activated carbon becomes saturated with sulfuric acid (product of sulfite oxidation) the rate of reaction is decreased. Hence there is insufficient time in the column to utilize all the oxygen available.

Adding a second column in series, identical to the first, produces an effluent with 16 mg/1 SO_2 (data in Appendix B, Tables B-27 through B-32). Thus it appears, with minor modifications, two filters in series with 25 cm activated carbon at a liquid loading of 8.8 ml/min per M^2 (50 ml/min) would oxidize the SO_2 .

A summary of the various combinations of design parameters used and the ability to remove the influent $S0₂$ are shown in Table 6 (see Appendix B, Tables B-33 through B-44). As shown, when aerating the column at 140 ℓ /hr a relationship develops, at zero SO₂ breakthrough, between carbon depth and liquid flow (see Appendix B, Tables B-34, B-36 , B-38 , B-40, B-43 , B-46). This proves to be a linear relationship as shown in Figure 18. Using the column with 50 cm of carbon and a flow rate of 150 ml/min for 24 hours, a carbon weight to liquid volume ratio of $5.5 \text{ g}/1$ may be computed. Thus with sufficient oxygen available, activated carbon is a far better catalyst than indicated by the 40 g/I ratio determined by the jar tests.

Assuming an 8 percent transfer efficiency between air and water, 63 ℓ /hr of air should be required to oxidize 500 mg/l SO₂ at a flow

Figure 17. SO_2 oxidation column observations.

Figure 18. Flow vs. carbon volume for zero SO_2 breakthrough (24 hr runs).

rate of 150 ml/min. Thus it was unexpected to see the column operated at 70 ℓ/nr of air fail. There appears to be several possible reasons. One reason is insufficient detention time in the column. In light of improved performance with increased air flow this explanation does not appear likely. Another reason is that the assumed 8 percent transfer efficiency is too high. This is tied to the air diffuser bubble size and air distribution in the column. Figures 19 and 20 shows the air distribution in a 9.0 cm diameter beaker. At 70 ℓ /hr the air bubbles rise straight up the center of the beaker whereas at $140 \ell/hr$ the air bubbles spread out through the entire column. Thus it would appear that the assumed 8 percent transfer efficiency at 70 ℓ /hr is incorrect. More efficient air distribution in a larger system may reduce the required air flow to theoretical values.

Throughout these experiments a milky colored precipitate would form in columns that failed. There is no apparent cause for the formation of this precipitate. The precipitate would form in samples taken from 60 to 720 minutes; dissolved oxygen levels were generally less than 4 mg/l; pH varied from 2.4 to 5.5; and SO_2 concentrations were greater than 4 mg/l. An electron microscopy scan of the precipitate showed the primary elements to be phosphorus and iron. This again gave no clue as to the cause of the precipitation formation. Because the precipitate did not form in samples from successful columns (i.e. no $SO₂$ breakthrough), investigation of this phenomenon was not pursued.

The column consisting of 50 cm activated cqrbon, an air flow of 140 t/hr, and a liquid flow of 150 ml/min was run for a period of 96 hours to determine long term catalytic abilities of the carbon (see Figure 21 and Appendix B, Table B-47). Breakthrough of SO_2 began after

Figure 19. Air distribution at 70 %/hr.

Figure 20. Air distribution at 140 ℓ /hr.

Figure 21. 96 hour column run.

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24 hours and increased (in a fluctuating manner) to 40 mg/l after 96 hours, the highest concentration recorded. The cause of the gradual failure is the self-poisoning of the carbon via saturation with sulfuric acid. The removal of the sulfuric acid is necessary for continued oxidation of S02. This may be accomplished by flushing the carbon with water (Komiyama and Smith 1975). To test this assumption, a column was run to failure (defined by effluent $S0₂$ values greater than 20 mg/l), then backwashed with water and the column restarted (see Figure 22 and Appendix B, Table B-48). Backwashing was accomplished by running tap water up through the column, expanding the carbon bed by 20 percent. Forty liters of water were used over a 20 minute period. Initial pH of the backwash water was 2.2; after 4 minutes the pH rose to 6.0. The final backwash pH was 6.8. This increase in pH indicates the flushing out of the acid.

Following backwashing, the carbon bed resettled to 110 percent of its original height. This is due to the strong inter-particle attraction exhibited by wet carbon. The first run failed after 10 hours. The second run, after backwashing, ran for 40 hours without failing (as defined earlier). The most probable cause for the improved performance after backwashing is the increased exposed surface area created by the bridging between carbon particles. Thus it may be concluded that backwashing removes the sulfuric acid and regenerates the catalytic properties of the activated carbon.

The fate of the sulfur species was examined during all 24 hour runs. The results during the 96 hour run are shown in Figure 21. Through the course of the run, 91 percent of the influent sulfur

Figure 22. Backwashed column results.

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species (+IV and +VI) were accounted for in the effluent. Causes of the missing sulfur may be the formation of dithionate, loss of $S0₂$ gas in the column, and inaccuracies in the sulfate data due to the analytical procedure used.

COST ANALYSIS

Costs for the sulfur dioxide oxidation system were developed based on reasonable limits in design criteria as shown in Table 7. The worst case design criteria is that developed by the bench scale column. The low surface loading in this case results in a very large filter surface area. By increasing the surface loading and increasing the carbon bed depth (maintaining the carbon volume), the filter surface area and cost may be greatly decreased. For a given carbon volume and flow rate, pilot plant testing must be conducted to optimize surface loading and carbon bed depth.

The worst case also assumes an air requirement equivalent to that used in the bench testing. The best case assumes an air requirement equal to theoretical values.

A capital cost summary for both cases is shown in Table 8. A generalized flow sheet for the S02 oxidation system is shown in Figure 23. The filter costs are based on a typical dual media filtration unit (see Appendix D). Included in the filter costs are the feed system, tankage, underdrain system, backwash pump and storage tank, building, and appurtenances necessary for complete operation. The large surface area required for the downflow contactor mode of operation, along with the need for enclosing the filters, makes this system extremely capital intensive.

Annual costs for the SO_2 oxidation system are shown in Table 9. The power costs include feed and backwash pumping, and blowers for aeration. Total power represents only 6-15 percent of the total annual costs indicating a very low-energy use system.

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Table 7. Summary of design criteria.

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Note: m^3/d \times 2.6417 \times 10^{-4} = mga1/daym^2 x 10.7639 = ft<sup>2</sup>
       m \times 3.2808 = ftm^3/m^2 d x 24.5424 = gal/ft<sup>2</sup> d
       m^3/h x 0.5886 = ft<sup>3</sup>/min
       kw \times 1.3410 = HP
```
Table 8. SO₂ oxidation system capital cost estimate.

aConstruction costs only.

Figure 23. Flow sheet for so_2 oxidation system.

Table 9. SO₂ oxidation system summary of annual costs.

a7 percent for 20 years, cost recovery factor = 0.09439 .

Labor and material costs were an average of values taken from EPA (1980) cost curves for dual media filtration and trickling filter operations. Labor costs were adjusted to a current rate of \$13.20 per man hour; material costs represent from 1.5-2.5 percent of the capital costs.

Table 10 compares the complete SO_2 disinfection process with other disinfection systems. The costs for the SO_2 disinfection process excluding the oxidation system, along with the other alternative disinfection processes were developed by Nielsen, Maxwell and Wangsgard-Montgomery Inc. (see Appendix D). As shown, when compared to other processes, the S02 disinfection process is capital intensive. Total operation and maintenance costs are also significantly higher than for other disinfection processes.

Table 10. Comparison of capital and operation and maintenance costs for various wastewater disinfection processes based on Total Coliform (TC) or Fecal Coliform (FC) standards.

aCosts developed by Nielsen, Maxwell and Wangsgard-Montgomery, Inc.

bTotal 802 disinfection process, including 802 oxidation system.

Costs were also developed for two different coliform discharge standards. The costs for the alternative disinfection systems increase significantly with a more stringent fecal coliform standard. This is due to much greater chemical costs required to meet the higher discharge standards. Larger chemical doses are not necessary with the $S0₂$ disinfection system, thus costs are not affected by the more stringent standards.

The costs for sulfur dioxide disinfection range from \$0.23 to \$0.73/1000 gallons treated CTable 11). Only for the most stringent coliform standard does the best case SO_2 system prove to be less costly than ozonation or ultraviolet radiation. When compared with other disinfection processes and coliform standards the SO_2 system is more expensive.

Table 11. Summary cost (¢/1000 gallons treated) comparison between sulfur dioxide disinfection and other alternative disinfection systems.

	$Standard =$ $2.2 \text{ FC}/100 \text{ m}1$		$Standard =$ 1000 TC/100 ml	
Process				
	3785	37850		3785 37850
	m^3/d	m^3/d	m^3/d	m^3/d
Chlorination-Dechlorination (without post aeration)	7.9	4.6	6.0	1.9
Chlorination-Dechlorination (with post aeration)	9.2	5.5	7.3	2.6
Chlorine Dioxide/SO ₂ Reduction	27.2	21.9	16.2	10.9
Ozonation	51.7	34.6	12.9	6.1
Ultraviolet Light	261.6	250.7	9.7	8.7
Best SO ₂ Case	40.5	23.2	40.5	23.2
Worst $SO2$ Case	72.9	46.5	72.9	46.5

Note: $\frac{c}{1000}$ gal x 0.264 = $\frac{c}{M^3}$.

SUMMARY AND CONCLUSIONS

This research dealt with the removal of the oxygen demand created in wastewater disinfected with sulfur dioxide at a concentration of 500 mg/l. The removal mechanism studied was catalyzed oxidation. Catalysts studied included transition metals (Fe++, Mn++, Co++), activated carbon (Calgon Filtrasorb 300), and a combination of the two. It was found that the metals, and activated carbon plus metals were very good catalysts for the oxidation of sulfur dioxide, to sulfate. However, the acidic nature of the disinfected wastewater (pH 2.6) dissolved the metals or caused them to desorb from the carbon. Activated carbon was also shown to be a good catalyst as long as sufficient oxygen levels were maintained. Results showed that the catalytic properties of activated carbon may be maintained over an extended period of time by backwashing the carbon to remove the sulfuric acid produced by the oxidation of sulfur dioxide.

The costs of sulfur dioxide disinfection range from \$0.23-\$0.73/ 1000 gallons treated. In general, this is much more costly than other disinfection processes.

Specific conclusions drawn from this research include:

1) The acidic nature of the disinfected wastewater (pH 2.6) will not allow use of transition metals as an oxidation catalyst due to excessive metal transport into solution.

2) Activated carbon does catalyze the oxidation of SO_2 in wastewater.

3) In a downflow contactor with sufficient oxygen, it was found that 5.5 g carbon/1 was necessary for complete SO_2 removal over a 24 hour period.

4) Twice the theoretical air flow was found necessary to provide sufficient oxygen for complete SO_2 oxidation, probably caused by poor air distribution in the column.

5) Self-poisoning of the carbon by sulfuric acid (the product of SO_2 oxidation) and/or reduced oxygen solubility in the sulfuric acid saturated column slowly reduced the catalytic effects of the activated carbon.

6) Backwashing the column removed the sulfuric acid and restored the catalytic properties of the activated carbon.

7) Without significant capital cost reductions, SO₂ disinfection cannot compete with other disinfection processes.

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ENGINEERING SIGNIFICANCE

The data collected in this study suggest a possible method for the oxidation of sulfur dioxide in wastewater. The development of wastewater disinfection processes, to replace chlorination, is needed in light of increasing evidence of adverse health affects created by chlorination. Sulfur dioxide has been shown to be an effective disinfectant; however, the oxygen demand created by aqueous sulfur dioxide must be eliminated prior to discharge. Oxidation is one means of accomplishing this task.

Activated carbon was shown to be an effective catalyst in the oxidation of sulfur dioxide, with sulfuric acid as a byproduct. The ease of operation of a trickling filter type reactor (downflow contactor) and the sample regeneration of the carbon via backwashing make the system worth further consideration. However a great deal of additional research is necessary to optimize the type of activated carbon used and the process design parameters. Hopefully this research will lead to significant reductions in the preliminary capital costs generated during this study.

RECOMMENDATIONS

- 1. Conduct pilot plant testing to refine the design parameters developed at bench scale including surface loading, backwashing, and air flows.
- 2. Further study the role of activated carbon as a catalyst.
- 3. Further study the fate of other wastewater constituents in the system.
- 4. Study different system configurations to help reduce costs (e.g., recycle filter effluent to reduce sulfur dioxide requirements).
- 5. Study several different commercial brands of activated carbon to determine how raw materials affect catalytic properties.
- 6. Other reactor types, such as a fluidized carbon bed, should be investigated in order to reduce the high costs associated with the downf1ow contactor arrangement.

LITERATURE CITED

- APHA. 1980. Standard methods for the examination of water and wastewater. 15th Ed. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, D.C. 1134 p.
- Brimblecombe, P., and D. J. Spedding. 1974. The reaction order of the metal ion catalyzed oxidation of sulfur dioxide in aqueous solution. Chemosphere 1:29-32.
- Bengtsson, S., and I. Bjeiles. 1975. Catalytic oxidation of sulphite in diluted aqueous solutions. Chemical Engineering Science 30: 1429-1435.
- Brodzinsky, R., S. G. Chang, S. S. Markowitz, and T. Novakov. 1980. Kinetics and mechanism for the catalytic oxidation of sulfur dioxide on carbon in aqueous suspensions. J. Phys. Chem. 84: 3354-3358.
- Chang, S. G., R. Brodzinsky, S. S. Markowitz, and T. Novakov. 1976-77. Catalytic oxidation of SO₂ on carbon in aqueous suspension. Atmospheric Aerosol Research, Annual Report, LBL 6819.
- Chen, T-I., and C. H. Barron. 1972. Some aspects of the homogeneous kinetics of sulfite oxidation. Ind. Engng. Chem. FundI. 11(4): 466-469.
- Coughanowr, D. R., and F. E. Krause. 1965. The reaction of SO_2 and 02 in aqueous solutions of Mn804. Ind. Engng. Chem. FundI. $4(1):61-66$.
- Eatough, D. J., W. P. Green, and L. D. Hansen. 1979. Oxidation of sulfite by activated charcoal. Lawrence Berkeley Lab J. 79(LBL-9037):131-132.
- EPA. 1979. Kinetics of sulfur dioxide in aqueous solution. EPA-600/ 7-79-030. 73 p.
- EPA. 1980. Innovative and alternative technology assessment manual. EPA-430/9-78-009.
- EPA. 1981. Sulfur dioxide oxidation reactions in aqueous solutions. PB81-l96834. 31 p.
- Fuller, E. C., and R. H. Crist. 1941. The rate of oxidation of sulfite ions by oxygen. J. Am. Chem. Soc. 63:1644-1650.
- Hesketh, H. E., and R. W. Potokar. 1977. Reduce SO₂ emissions using fly ash slurries. Proc. Environ. Eng. Sci. Conf., 6th Annual, Univ. of Louisville, Louisville, KY.

- Komiyama, H., and J. M. Smith. 1975. Sulfur dioxide oxidation in slurries of activated carbon. A1ChE J. 21(4):664-670.
- Novakov, T., and S. G. Chang. 1975. Catalytic oxidation of SO_2 on carbon particles. A1ChE Symposium Series 72(156):255-262.
- Penkett, S. A., B. M. R. Jones, K. A. Brice, and A. E. J. Eggleton. 1979. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater. Atmospheric Env. 13:123-137.
- Reynolds, J. H., and V. D. Adams. 1979. Evaluation of sulfur dioxide disinfection. Report to International Environmental, Inc., Salt Lake City, UT.
- Schmidt, M. 1972. Fundamental chemistry of sulfur dioxide removal and subsequent recovery via aqueous scrubbing. Int. J. Sulfur Chem., Part B. 7(1):11-19.
- Seaburn, J. T., and A. J. Engel. 1973. Sorption of sulfur dioxide by suspension of activated carbon in water. A1ChE Symposium Series 69(134):71-75.
- Siedlewski, J. 1965. The mechanism of catalytic oxidation on activated carbon. The role of free carbon radicals in the oxidation of S02 to S03. Int. Chem. Engng. 5(4):608-612.
- Tiwari, B. L., J. Kolbe, and H. W. Hayden, Jr. 1979. Oxidation of ferrous sulfate in acid solution by a mixture of sulfur dioxide and oxygen. Metallurgical Trans. 10B:607-6l2.
- Watkins, J. P. 1977. Controlling sulfur compounds in wastewaters. Chem. Engng. 84(22):61-65.

APPENDICES \sim \sim

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Appendix A

Manufacturer Information

Activated carbon characteristics

Description.* Filtrasorb activated carbons are manufactured from select grades of bituminous coal to produce a high density, high surface area, durable granular product. They are capable of withstanding the abrasion and dynamics associated with repeated react ivation, hydraulic transport, backwashing, and mechanical handling. Filtrasorb carbons wet readily and do not float, thus minimizing loss during backwash operations.

Physical properties.

Specifications.

*Calgon Corporation, Product Bulletin 27-33a.
Manufacturers addresses

- 1) Ca1gon Corp. Activated Carbon Division P.o. Box 1346 pittsburgh, PA 15230
- 2) Alfa Products Thiokol/Ventron Division 152 Andover St. Danvers, MA 01923

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 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

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Appendix B

Raw Data

 $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$

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Note: 62

- 1. The following tables and graphs may show air flow in units of cubic feet per hour. The conversion to liters per hour is: $CFH \times 28.32 =$ ℓ /hr.
- 2. All sulfur specie concentrations are reported as $mg/1$ as SO_2 .

Table B-1. SO_2 oxidation jar test--4/22.

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	Column Media = $Mn \cdot$ Alumina	Initial Metal = N/A					
	Final Metal	\equiv					
	Initial Feed Soln.					Final Feed Soln.	
	$DO = 6.2$				DO 0	$= 5.7$	
	$pH = 2.7$					$pH = 2.5$	
		$SO_2 = 532 \text{ mg}/1$				$S0_2 = 496$ mg/1 $SO_4^{\equiv} = 161$ mg/1	
	$SO_4^- = 69$ mg/1 $Mn = \langle 4 \text{ mg}/1$						
			Column Data: Air Flow = 15-20 CFH				
Time Min.	D ₀	pH	SO ₂ mg/1	SO_4 as $S02$	$_{\rm F1ow}$ ml/min	Metal mg/1	
$\mathbf{0}$		0.2 3.6	108	176	55	39	
10	0.4 3.3		108	241	55	76	
20		0.2 3.2	108	267	54	91	
30		0.6 3.1	108	257	52	96	
40	0.5 3.1		104	233	52	99	
50		0.1 3.1	100	257	51	105	
60		0.1 3.1	100	242	53	100	
90		0.1 3.1	104	303	51	105	
120		0.1 3.0	100	312	51	105	
150	0.1	2.9	80	295	43	110	

Table B-3. SO_2 oxidation column observations--7/19.

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Table B-4. SO₂ oxidation column observations--7/23.

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Column Media = Co, Ni, Fe\text{-}Alumina
      Initial Metal = N/A<br>Final Metal =
      Final Metal
Initial Feed Soln.<br>
D0 = 5.0 Final Feed Soln.<br>
D0 = 5.2\begin{array}{rcl} \text{DO} & = & 5.0 \\ \text{pH} & = & 2.6 \end{array} \begin{array}{rcl} \text{DO} & = & 5.2 \\ \text{pH} & = & 2.4 \end{array}pH = 2.6 pH = 2.4
      SO_2 = 540 \text{ mg}/1 SO_2 = 488 \text{ mg}/1SO_4^{\pm} = 46 mg/1 as SO_2 SO_4^{\pm} = 37 mg/1 as SO_2Co = \langle 3 \text{ mg}/1 \rangleNi = 16 \mu g/lFe = 49 \text{ µg}/1
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Column Data: Air Flow = 15-20 CFH

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Table $B-5$. SO_2 oxidation column observations--7/23.

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Table B-6. Preliminary assessment of oxidation catalysts--7/30.

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Column Conditions:<br>Feed Rate =
                    = 50 ml/min.
    Medium Depth = 25 cm
    Feed Soln. pH = 2.5-2.9<br>Air Flow = 7.2-9.5= 7.2-9.5 \ell/min.<br>= 3 hrs.
    Run Time
```


*Oxidative Capacity (Effluent SO_2 Concentration): Good < 50 mg $SO_2/1$; Fair $\langle 100 \text{ mg } SO_2/1$; $SO_2/1$; Poor $> 100 \text{ mg } SO_2/1SO_2/1$ Effluent DO: Good ≥ 2 mg/l; Poor ≤ 2 mg/l Effluent pH: Good ≥ 6.5 ; Poor ≤ 6.5 Effluent Metals: Good ≤ 1 mg/l; Fair \leq 5 mg/l; Poor > 5 mg/l

Raw iron (1/4" nuts) was placed in bottom of 4000 ml beaker. 1700 ml sewage with 500 mg/1 SO_2 added to beaker and aerated at 15-20 CFH. pH and DO monitored continuously. Samples taken at 1 min. intervals.

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Table B-I0. S02 oxidation column observations--8/14.

*One of the round clear pellets or crystals passed through and must have clogged the flow momentarily.

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Table B-12. S02 oxidation column observations--8/20.

Table B-13. S02 oxidation column observations--B/27.

Note: At 720, add 100 ml H_2 SO₃, Feed SO₂ = 488 mg/1

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Note: At 660 , add $48 \text{ ml } H_2$ 803 , Feed $802 = 512 \text{ mg}/1$ At 900, add 41 ml H_2 so₃, Feed So₂ = 512 mg/1 At 1260 , add 26 ml H_2 so₃, Feed So₂ = 520 mg/1

Table B-14. SO_2 oxidation column observations--8/29.

Note: At 600 , Add 65 ml H_2 SO₃, Feed SO₂ = 492 mg/1 At 1260 Add 22 ml H_2 SO₃, Feed SO₂ = 488 mg/1 \equiv

Column Media = GAC, 25 cm Initial Metal = N/A
Final Metal = Final Metal Initial Feed Soln.
 $D0 = 6.5$

Final Feed Soln.
 $D0 = 5.6$ $DO = 6.5$ DO = $pH = 2.6$ pH = 2.6 $SO_2 = 504 \text{ mg}/1$
 $SO_4 = 46 \text{ mg}/1$ as SO_2
 $SO_4 = 46 \text{ mg}/1$ as SO_2
 $SO_4 = 71 \text{ mg}/1$ as SO_2 SO_4 = 46 mg/l as SO_2 SO_4 = 71 mg/l as SO_2 $\Delta 1k = 277 \text{ mg}/1$ Column Data: Air Flow = 0 CFH Time DO pH SO_2 SO_4^* Flow Comments
Min. $mg/1$ as SO_2 ml/min ml/min 10 7.5 7.5 0 202 49 20 6.6 6.6 0 264 52 30 5.6 4.7 0 313 49 Cloudy 60 4.4 2.6 32 391 50 Cloudy 90 3.6 2.4 56 440 50 Cloudy 120 3.8 2.2 68 481 49 Cloudy 180 3.5 2.1 100 473 51 240 4.2 2.1 124 477 48 300 3.7 2.1 152 452 50 360 3.6 2.1 152 477 51 420 3.8 2.0 144 469 50 Feed $SO_2 = 512 \text{ mg}/1$
480 3.8 2.0 156 444 50 480 3.8 2.0 156 444 50 540 4.3 2.0 160 461 50 600 4.5 2.0 168 456 47 660 4.4 2.0 160 440 51 720 4.4 2.0 156 428 50 Feed $SO_2 = 472 \text{ mg}/1$
780 4.4 2.0 160 436 49 780 4.4 2.0 160 436 49 840 4.0 2.0 148 420 47 900 3.9 2.05 160 399 50 Feed $SO_2 = 488 \text{ mg}/1$
960 4.1 2.0 152 395 47 960 4.1 2.0 152 395 47 1020 4.1 2.0 156 428 49 1020 4.1 2.0 156 428 49
1080 4.2 2.0 148 346 50 Feed $S0_2 = 460$ mg/1
1140 4.0 2.05 164 354 52 1140 4.0 2.05 164 354 52 1200 4.3 2.05 160 309 50 1260 4.0 2.05 172 313 54 Feed $SO_2 = 468 \text{ mg}/1$
1320 4.2 2.0 152 272 50 1320 4.2 2.0 152 272 50 1380 4.2 2.1 172 321 60 1440 4.3 2.05 136 48

Figure B-1. SO₂ oxidation column observations.

Table B-18. 502 oxidation column observations--9/l6.

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Figure B-2. SO₂ oxidation column observations.

Table B-19. SO₂ oxidation column observations--9/18.

 $Column Media = GAC, 25 cm$ $Initial$ Metal = N/A Final Metal = Initial Feed Soln. Final Feed Soln. $\begin{array}{rcl} \text{DO} & = & 5.5 \\ \text{pH} & = & 2.7 \end{array}$ $\begin{array}{rcl} \text{DO} & = & 4.8 \\ \text{pH} & = & 3.0 \end{array}$ pH = 2.7
 $SO_2 = 508 \text{ mg}/1$ pH = 3.0
 $SO_2 = 448 \text{ mg}/1$ $SO_2 = 508 \text{ mg}/1$
 $SO_4 = 46 \text{ mg}/1$ as SO_2
 $SO_4 = 66 \text{ mg}/1$ as SO_2
 $SO_4 = 66 \text{ mg}/1$ as SO_2 $SO_4 = 46$ mg/l as SO_2 $Alk = 272$ Column Data: Air Flow = 0 CFH Time DO pH SO_2 SO_4^{\pm} Flow Comments Time DO pH SO_2 SO_4 Flow
Min. $mg/1$ as SO_2 ml/min 10 6.2 8.4 4 182 51 20 5.5 7.7 0 248 49 30 4.8 4.1 0 298 51 Cloudy 60 3.0 2.6 44 389 50 Cloudy 90 2.6 2.5 112 381 48 Cloudy 120 0.1 2.5 192 369 50 Cloudy 180 0.1 2.6 304 298 51 240 0.1 2.6 336 286 50 300 0.1 2.7 376 257 51 360 0.1 2.7 388 240 53 420 0.1 2.7 396 257 50 480 2.3 2.8 392 257 51 Feed $SO_2 = 484 \text{ mg}/1$
540 0.1 2.8 348 232 50 540 0.1 2.8 348 232 50 600 0.1 2.9 360 228 50 660 0.1 2.9 400 207 49 720 0.1 2.8 412 198 52 Feed $SO_2 = 460$ mg/1
780 2.5 2.9 384 186 50 780 2.5 2.9 384 186 50 840 3.6 2.9 356 194 49 900 2.7 2.9 380 174 47 Feed $SO_2 = 464$ mg/1
960 3.1 3.0 392 157 50 960 3.1 3.0 392 157 50 1020 3.3 3.0 396 149 50 1080 3.4 3.1 376 140 50 Feed $SO_2 = 452 \text{ mg/l}$
1140 3.2 3.1 372 140 49 1140 3.2 3.1 372 140 49 1200 2.5 3.1 368 124 50 1260 2.7 3.1 348 120 53 Feed $SO_2 = 408 \text{ mg}/1$
1320 2.8 3.0 368 107 48 Add 29 ml H₂SO₃ 1320 2.8 3.0 368 107 48 Add 29 ml H₂ SO₃
1380 2.5 2.9 376 95 53 Feed SO₂ = 500 1380 2.5 2.9 376 95 53 Feed $SO_2 = 500$ mg/l
1440 2.6 2.8 392 107 52 1440 2.6 2.8 392 107 52

Figure $B-3$. SO_2 oxidation column observations.

Figure B-4. SO₂ oxidation column observations.

Column Media = GAC , 25 cm Initial Metal = N/A Final Metal = Initial Feed Soln. This rinal Feed Soln. $DO = 6.1$
 $pH = 2.55$
 $pH = 2.7$ pH = 2.55
 SO_2 = 552 mg/1
 SO_4 = 42 mg/1 as SO_2
 SO_4 = 42 mg/1 as SO_2
 SO_4 = 68 mg/1 as SO_2 $SO_2 = 552 \text{ mg}/1$ $SO_2 = 436 \text{ mg}/1$ $SO_4^{=}=$ 42 mg/1 as SO_2 80 $\frac{1}{4}$ 80 $\frac{1}{4}$ 88 mg/1 as SO_2 Column Data: Air Flow = 0 CFH Time DO pH SO_2 SO_4^{\pm} Flow Comments Time DO pH SO_2 SO_4^{\pm} Flow
Min. $mg/1$ as SO_2 m1/min 15 6.7 6.9 0 320 48 30 5.2 4.3 24 410 52 60 3.5 2.7 96 447 49 90 3.0 2.5 168 402 48 120 2.5 2.5 256 349 49 180 0.1 2.45 320 272 50 240 0.1 2.5 356 235 50 300 0.1 2.45 384 202 50 360 0.1 2.4 408 186 51 420 3.0 2.45 432 157 49 480 2.4 2.4 424 153 49 540 2.0 2.4 408 143 49 600 2.3 2.4 432 133 50 660 3.1 2.4 456 123 48 720 4.1 2.4 452 121 50 Feed $50₂ = 500$ mg/1
 780 2.1 2.4 416 137 48 780 2.1 2.4 416 137 48 840 2.4 2.4 412 110 50 900 2.3 2.4 432 108 49 Feed $SO_2 = 504$ mg/1
960 3.1 2.45 424 92 49 960 3.1 2.45 424 92 49 1020 3.3 2.4 436 90 50 1080 3.2 2.45 440 88 50 Feed $S0_2 = 500$ mg/1
1140 3.0 2.45 436 94 50 1140 3.0 2.45 436 94 50 1200 2.6 2.45 436 106 50 1260 2.9 2.5 412 108 48 Feed $50₂ = 476$ mg/1
1320 3.1 2.5 400 88 48 1320 3.1 2.5 400 88 48 1380 2.8 2.5 400 84 48 1440 2.7 2.5 396 96 51

Table B-21. SO_2 oxidation column observations--9/23.

Note: Inlet change, extend tube directly to surface of carbon

Figure B-5. SO₂ oxidation column observations.

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Table B-22. SO₂ oxidation column observations--9/28.

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Figure B-6. SO₂ oxidation column observations.

 $\label{eq:2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$

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Figure B-7. SO₂ oxidation column observations.

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Table B-24. S02 oxidation column observations--10/2.

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Table B-25. SO_2 oxidation column observations--10/5.

Column Media = GAC, 25 cm Initial Metal $= N/A$ Final Metal $=$ Initial Feed Soln.
 $D0 = 6.6$
 $D0 = 5.7$ $\overline{DO} = 6.6$
 $\overline{DO} = 5.7$
 $\overline{PH} = 2.7$
 $\overline{PH} = 2.6$ pH = 2.7 pH = 2.6
 $SO_2 = 520 \text{ mg}/1$ $SO_2 = 480$ $SO_2 = 520 \text{ mg}/1$
 $SO_4 = -$
 $SO_4 = -$
 $SO_4 = 52 \text{ mg}/1$ SO_4 = 52 mg/l as SO_2 Column Data: Air Flow $=$ 0 CFH Time DO pH SO_2 SO_4 Flow Comments Min. $mg/1$ as SO_2 ml/min 15 8.4 9.1 0 98 46 30 7.9 9.0 0 146 47 60 6.2 8.8 0 220 48 90 5.1 7.6 0 253 49 120 4.1 6.4 0 277 49 Cloudy 180 3.6 3.2 12 318 50 Cloudy 240 3.2 2.7 24 351 51 Cloudy 300 4.1 2.5 64 368 51 Cloudy 360 3.3 2.5 100 355 49 Cloudy 420 2.9 2.5 132 335 49 480 2.9 2.5 156 310 49 540 2.4 2.45 172 302 50 600 2.3 2.4 184 294 50 660 2.4 2.4 200 286 51 720 2.6 2.4 208 286 50 Feed 50 = 496 mg/l
 780 2.6 2.4 204 294 51 780 2.6 2.4 204 294 51 840 2.7 2.45 228 269 50 900 2.6 2.4 232 261 51 Feed $SO_2 = 476 \text{ mg}/1$
960 4.3 2.35 228 253 51 960 4.3 2.35 228 253 51 1020 1.9 2.6 224 236 50 1080 3.8 2.4 236 232 50 Feed $S0_2 = 484 \text{ mg}/1$
1140 2.8 2.4 244 236 50 1140 2.8 2.4 244 236 50 1200 3.7 2.4 240 51 1260 3.5 2.4 240 212 52 Feed $SO_2 = 452$ mg/l 1320 3.6 2.4 240 212 52 Add 23 ml H₂SO₃
1380 3.3 2.35 244 203 53 Feed SO₂ = 508 1 1380 3.3 2.35 244 203 53 Feed $SO_2 = 508 \text{ mg}/1$
1440 3.2 2.3 260 199 51 1440 3.2 2.3 260 199 51

Figure B-8. SO₂ oxidation column observations.
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Figure B-9. SO_2 oxidation column observations.

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Figure B-10. SO_2 oxidation column observations.

*Secondary feed SO_2 , mg/1

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Figure B-11. SO₂ oxidation column observations.

Column Media = GAC, 25 cm, primary column Initial Metal = N/A Final Metal = Initial Feed Soln.
 $D0 = 5.1$ Final Feed Soln. $DO = 5.1$ $DO = 4.2$
 $pH = 2.6$ $pH =$ $pH = 2.7$ $SO_2 = 500$ mg/1 $SO_2 = 488$ mg/1 SO_4^{2} = 49 mg/1 as SO_2 $SO_4^{\pm} = 62 \text{ mg}/1 \text{ as } SO_2$ Column Data: Air Flow = 0 CFH DO S02 Time pH SO_4 ^{$\overline{}$} Flow Comments $mg/1$ as $SO₂$ Min. ml/min 15 4.7 9.3 o 50 1.0 6.8 40 54 60 208 48 Cloudy 90 0.6 6.5 72 5.9 188 52 180 2.0 240 3.2 5.3 216 293 50 Cloudy 300 3.1 3.7 196 50 360 3.0 184 293 53 Cloudy 0.1 420 0.1 2.8 188 51 480 0.1 2.6 208 285 54 Cloudy 540 0.1 2.6 216 50 Feed $SO_2 = 508$ mg/1 0.1 2.5 204 600 277 49 660 **0.1** 2.5 228 49 720 0.1 2.5 240 269 54 Feed $SO_2 = 508$ mg/1 780 0.1 2.4 49 208 840 2.4 216 50 **0.1** 285 2.4 50 Feed $SO_2 = 480$ mg/1 900 0.1 240 960 0.1 2.35 236 50 301 2.3 1020 0.1 224 45 50 Feed $SO_2 = 476$ mg/1 1080 0.1 2.3 232 281 1140 0.7 2.4 224 52 1200 2.4 2.4 248 269 51 1260 2.9 2.4 256 53 Feed $SO_2 = 456$ mg/1 1320 3.3 2.3 248 244 55 Add 18 ml H₂S03
54 Feed S0₂ = 496 t 1380 3.5 2.3 248 Feed $SO_2 = 496$ mg/1 228 54 1440 3.3 2.3 248

Table B-29. SO₂ oxidation column observations--10/12.

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Figure B-12. SO_2 oxidation column observations.

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*Secondary feed SO_2 , mg/l

Note: Samples 300-780 were cloudy

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Figure B-13. SO₂ oxidation column observations.

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Table B-31. SO₂ oxidation column observations--10/14.

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Figure B-14. SO₂ oxidation column observations.

*Secondary feed SO_2 , mg/1

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Figure $B-15$. SO_2 oxidation column observations.

Column Media = GAC , 50 cm Initial Metal = N/A Final Metal $=$ Initial Feed Soln.
 $D0 = 4.3$

Final Feed Soln.
 $D0 = 3.4$ $\begin{array}{ccc} \text{DO} & = & 4.3 \\ \text{pH} & = & 2.6 \end{array}$ DO = pH = 2.6 pH = 2.6
 $SO_2 = 532 \text{ mg}/1$ $SO_2 = 460$ $SO_2 = 460$ mg/l
 $SO_4 = 53$ mg/l as SO_2 SO_4^{2} = 49 mg/l as SO_2 Column Data: $Air Flow = 0 CFH$ Time DO pH SO_2 SO_4 Flow Comments
Min. $mg/1$ as SO_2 $m1/min$ as SO_2 ml/min 15 6.8 9.0 0 51 60 6.1 9.0 0 81 54 90 5.7 8.9 0 49 120 4.9 8.8 0 158 50 180 3.7 6.7 0 50 240 3.7 5.5 0 266 50 Cloudy 300 3.5 3.0 12 50 360 3.2 2.8 16 330 50 Cloudy 420 2.7 2.7 40 50 480 1.6 2.6 56 338 50 Cloudy 540 1.6 2.6 68 50 Feed 50 Feed 50 = $512 \text{ mg}/1$
600 0.1 2.5 76 361 50 Cloudy 600 0.1 2.5 76 361 50 Cloudy 660 0.1 2.5 84 51 720 0.1 2.45 88 361 50 Cloudy 780 0.1 2.4 96 50 840 0.1 2.35 100 330 51 900 0.1 2.4 108 50 Feed $SO_2 = 480$ mg/1
960 0.1 2.4 104 330 49 960 0.1 2.4 104 330 49 1020 0.1 2.3 112 50 1080 0.1 2.3 116 338 50 Feed $SO_2 = 464$ mg/1
1140 0.1 2.3 120 50 Add 18 ml H₂SO₃ 1140 0.1 2.3 120 50 Add 18 ml H_2 SO₂ = 492 Feed $SO_2 = 492$ mg/1 1260 1320 2.0 2.3 156 286 50 1380 3.0 2.3 188 49 1440 3.1 2.3 192 258 51

Table B-33. SO₂ oxidation column observations--10/16.

Figure B-16. SO₂ oxidation column observations.

Table B-34. SO₂ oxidation column observations--10/19.

 $Column Media = GAC, 25 cm$ $Initial$ Metal = N/A Final Metal = Initial Feed Soln. Final Feed Soln. $DO = 4.2$ 3.5 $DO =$ pH = 2.7
 $SO_2 = 492 \text{ mg}/1$ pH = 2.75
 $SO_2 = 492 \text{ mg}/1$ $SO_2 = 460 \text{ g}$ $SO_2 = 460$ mg/l
 $SO_4 = 59$ mg/l as SO_2 $SO_4^{2}= 49 \text{ mg}/1 \text{ as } SO_2$ Column Data: Air Flow = 5 CFH Time DO pH SO_2 SO_4 Flow
Min. $mg/1$ as SO_2 ml/min Time DO pH SO_2 SO_4^{\pm} Flow Comments 15 6.4 8.7 0 49 60 6.4 8.6 0 173 52 90 5.6 7.1 0 50 120 5.5 4.7 0 254 50 180 5.15 2.9 0 50 240 5.0 2.7 0 343 51 300 5.1 2.55 0 51 360 5.1 2.4 0 392 50 420 5.2 2.4 0 51 480 5.4 2.3 0 408 51
540 5.4 2.3 0 50 Feed SO₂ = 468 mg/l
600 5.5 2.25 0 449 51 Add 34 ml H₂SO₃ 480 5.4 2.3 0 408 51 5.5 2.25 0 449 51 Add 34 ml H₂SO₃
5.6 2.2 0 51 Feed SO₂ = 524; 5.6 2.2 0
 720 5.5 2.2 0 465 50 $5 \text{ e} \cdot \text{e} \cdot \text{S} \cdot \text{S}$ 720 5.5 2.2 0 465 50 Feed $SO_2 = 464 \text{ mg}/1$
780 5.7 2.2 0 51 Add 32 ml H₂SO₃ 780 5.7 2.2 0
840 5.7 2.15 0 498 50 Feed $SO_2 = 520$ 840 5.7 2.15 0 498 50 Feed SO₂ = 520 mg/1 900 5.8 2.1 0 50 Feed $SO_2 = 488 \text{ mg}/1$ 960 5.8 2.1 0 506 50 1020 5.8 2.1 0 50 1080 5.9 2.1 0 510 50 Feed $SO_2 = 492 \text{ mg/l}$
1140 5.9 2.1 0 49 1140 5.9 2.1 0 49 1200 5.9 2.1 0 502 48 1260 5.9 2.1 0 49 Feed $SO_2 = 488 \text{ mg}/1$ 1320 6.1 2.1 0 498 52 1380 6.0 2.1 0 52 1440 6.0 2.1 0 461 52

Figure $B-17$. SO_2 oxidation column observations.

Table B-35. SO₂ oxidation column observations--10/21.

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Figure B-18. SO₂ oxidation column observations.

Table B-36. SO₂ oxidation column observations--10/23.

 $Column Media = GAC, 35 cm$ Initial Metal = N/A Final Metal = Initial Feed Soln.
 $D0 = 5.2$
 $D0 = 4.5$ $DO = 4.5$
pH = 2.5 pH = 2.6 pH = 2.5
 $SO_2 = 488 \text{ mg}/1$ $SO_2 = 460 \text{ mg}/1$ $SO_2 = 488 \text{ mg}/1$ $SO_2 = 460 \text{ mg}/1$ SO_4^{\pm} = 45 mg/1 as SO_2 SO₄ = 62 mg/1 as SO_2 Column Data: $Air Flow = 5 CFH$ Time DO pH SO₂ SO₄^{p} Flow Comments Min. $mg/1$ as SO_2 ml/min 15 7.2 9.0 a 102 30 7.2 8.9 a 100 60 6.9 8.6 0 204 102 90 6.4 6.9 0 100 120 5.2 3.6 0 277 100 180 5.1 2.6 0 98 240 5.4 2.4 0 391 100 300 5.5 2.3 0 100 360 5.6 2.2 0 440 100 420 5.7 2.2 0 100 480 5.8 2.1 0 456 100 540 5.8 2.1 a 100 600 5.9 2.1 a 488 100 660 6.0 2.1 0 100 $\begin{array}{cccc} 660 & 6.0 & 2.1 & 0 & 100 \ 720 & 6.0 & 2.05 & 0 & 501 & 100 \end{array}$ Feed $\begin{array}{cccc} 502 & 452 \text{ mg}/1 \end{array}$ 780 6.0 2.05 0
840 5.8 2.0 0 521 100 Feed SO₂ = 512 840 5.8 2.0 0 521 100 Feed $S0_2 = 512$ mg/1 900 5.7 2.0 0 100 Feed $SO_2 = 524 \text{ mg}/1$ 960 5.6 2.0 0 533 100 1020 5.7 2.0 0 100 1020 5.7 2.0 0
1080 5.7 2.0 0 533 100 Feed $SO_2 = 540$ mg/1
1140 5.8 2.0 0 100 1140 5.8 2.0 0 100 1200 5.7 1.95 0 529 100 1260 5.7 1.95 0 100 Feed $S0_2 = 518$ mg/1 1320 5.7 2.0 0 537 100 1380 5.8 2.0 0 100 1440 5.8 2.0 0 501 100

Figure B-19. SO₂ oxidation column observations.

Table B-37. SO₂ oxidation column observations--10/26.

Column Media = GAC , 35 cm Initial Metal = N/A Final Metal $=$ Initial Feed Soln. Final Feed Soln. $\overline{DO} = 5.6$ $\overline{DO} = 4.1$ pH = 2.7
 $SO_2 = 496 \text{ mg}/1$ pH = 2.7
 $SO_2 = 496 \text{ mg}/1$ $SO_2 = 456$ $SO_2 = 496 \text{ mg}/1$
 $SO_4 = 45 \text{ mg}/1$ as SO_2
 $SO_4 = 60 \text{ mg}/1$ $SO_4^{==}$ 60 mg/l as SO_2 Column Data: Air Flow = 5 CFH Time DO pH SO_2 SO_4^{\pm} Flow Comments Min. $mg/1$ as SO_2 m1/min 15 6.6 8.7 0 139 150 30 6.0 7.7 0 154 60 4.3 3.3 8 326 150 Cloudy 90 3.8 2.7 20 150 120 3.8 2.5 30 407 150 Cloudy 180 3.3 2.35 56 150 240 3.2 2.3 64 448 150 300 2.9 2.2 78 150 360 3.1 2.2 82 448 150 420 3.1 2.2 88 150 480 3.2 2.2 80 460 150 540 3.3 2.2 84 150 600 3.5 2.2 104 448 147 660 3.7 2.2 108 150 720 3.6 2.15 112 440 150 Feed $SO_2 = 492 \text{ mg}/1$
780 3.6 2.15 108 150 780 3.6 2.15 108 150 840 3.6 2.15 112 423 150 900 3.3 2.15 120 150 Feed $SO_2 = 508 \text{ mg}/1$
960 3.1 2.15 128 411 150 960 3.1 2.15 128 411 150 1020 3.1 2.15 120 150 1080 3.1 2.15 116 411 150 Feed $SO_2 = 504$ mg/1
1140 3.0 2.15 116 150 1140 3.0 2.15 116 150 1200 3.0 2.15 112 383 150
1260 3.0 2.15 112 150 Feed SO₂ = 488 mg/1
1320 3.2 2.15 108 383 150 1200 3.0 2.15 112 383 150 1320 3.2 2.15 108 383 150 1380 3.3 2.1 104 150 1440 3.6 2.1 108 350 150

Figure B-20. SO₂ oxidation column observations.

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Figure $B-21$. SO_2 oxidation column observations.

Table B-39. SO₂ oxidation column observations--10/30.

Column Media = GAC , 50 cm Initial Metal = N/A Final Metal Initial Feed Soln.
 $D0 = 6.3$
 $D0 = 4.6$ $\begin{array}{rcl} \text{DO} &= 6.3 \\ \text{pH} &= 2.5 \end{array}$ $\begin{array}{rcl} \text{DO} &= 4.6 \\ \text{pH} &= 2.6 \end{array}$ $pH = 2.6$ $SO_2 = 536$ mg/1
 $SO_4 = 45$ mg/1 as SO_2
 $SO_4 = 65$ mg/1 as SO_2
 $SO_4 = 65$ mg/1 as SO_2 SO_4 = 45 mg/l as S02 Column Data: Air Flow = 5 CFH Time DO pH SO_2 SO_4 $Flow$ Comments
Min. $mg/1$ as SO_2 ml/min as SO_2 ml/min 15 7.6 8.8 0 110 171 30 7.2 8.4 0 176 60 5.1 5.9 0 285 176 Cloudy 90 4.4 2.85 0 176 120 4.1 2.5 4 383 176 Cloudy 180 4.0 2.2 22 174 240 3.8 2.2 34 456 174 300 3.8 2.1 44 174 360 4.3 2.1 50 456 174 420 4.1 2.1 54 171 480 3.8 2.1 64 456 171 480 3.8 2.1 64 456 171
540 3.2 2.1 68 176 Feed SO₂ = 512 mg/l
600 3.1 2.1 76 460 176 600 3.1 2.1 76 460 176 660 3.6 2.1 76 176 720 3.4 2.05 80 436 176 Feed $SO_2 = 512$ mg/1
780 3.3 2.05 80 175 780 3.3 2.05 80 175 840 3.2 2.05 80 436 175 900 3.5 2.05 84 175 960 3.4 2.05 84 415 175 1020 3.7 2.05 80 176 1080 3.1 2.05 80 407 174 1140 3.6 2.05 76 172 1140 3.6 2.05 76 172
1200 3.7 2.05 76 407 172 Feed SO₂ = 496 mg/l 1260 3.8 2.05 72 175 1320 3.6 2.05 68 415 175 1380 4.1 2.05 66 172 1440 3.2 2.05 62 391 169

Figure B-22. SO₂ oxidation column observations.

Table B-40. 802 oxidation column observations--11/2.

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Figure B-23. $SO₂$ oxidation column observations.

Table B-41. SO₂ oxidation column observations--11/4.

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Figure B-24. SO₂ oxidation column observations.

Table B-42. SO₂ oxidation column observations--11/6.

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Column Media = Anthracite, 50 \text{ cm}Initial Metal = N/AFinal Metal = 
Initial Feed 8oln. 
    DO = 6.2pH = 2.8SO_2 = 496 mg/1
    SO_4^{\frac{2}{m}} = 45 \text{ mg}/1 \text{ as } SO_2Column Data: Air Flow = 5 CFH 
                                       Final Feed 
8oln. 
                                            DO = 5.7pH = 2.75SO_2 = 484 \text{ mg}/1<br>SO_4 = 62 \text{ mg}/1 \text{ as } SO_2SO_2 = 484 \text{ mg}/1Time DO pH SO_2 SO_4^= Flow Comments<br>Min. mg/1 as SO_2 ml/minm1/min15 0.5 2.5 216 476 150 Yellow Effluent 
  30 0.1 2.5 304 360 150 
  60 0.8 2.6 360 299 154 
  90 3.0 2.7 384 308 146 Clear 
 120 4.2 2.7 392 243 146 
 180 6.6 2.7 400 211 146 
 240 6.6 2.7 400 219 146 
 300 
 360 
 420 
 480 
 540 
 600 
 660 
 720
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Note: Run ended at 240 due to high breakthrough

Figure $B-25$. SO_2 oxidation column observations.

Note: Sewage from 8a1t Lake City

Figure B-26. SO_2 oxidation column observations.
Column Media = GAC, 35 em Initial Metal = N/A Final Metal $=$ Initial Feed Soln. The Soln. Final Feed Soln. $DO = 6.0$ $DO = 4.8$ pH = 2.6 pH = 2.7
 $SO_2 = 568 \text{ mg}/1$ $SO_2 = 456 \text{ mg}/1$ $SO_2 = 568 \text{ mg}/1$ SO₂ = 456 mg/1 $SO_4^{=}=$ 45 mg/1 as SO_2 SO₄^{$=$} 55 mg/1 as SO_2 $Alk = 271$ mg/1 Column Data: Air Flow = 7.5 CFH Time DO pH SO_2 SO_4 Flow Comments
Min. $mg/1$ as SO_2 $m1/min$ as SO_2 m1/min 15 7.4 8.6 0 172 150 30 6.9 7.6 0 152 60 5.2 5.0 0 284 150 Cloudy 90 4.5 3.1 4 152 120 4.8 2.7 0 372 146 Cloudy 180 5.4 2.3 8 154 240 4.2 2.2 18 480 154 300 4.8 2.2 22 146 360 3.7 2.15 30 505 148 420 3.7 2.15 36 146 480 3.7 2.1 44 489 148 540 4.1 2.1 40 152 Feed $SO_2 = 532 \text{ mg}/1$
600 4.5 2.1 48 480 150 600 4.5 2.1 48 480 150 660 4.2 2.1 44 150 720 4.2 2.1 44 150
 720 3.9 2.1 44 465 150 Feed SO₂ = 508 mg/1
 780 3.7 2.1 48 150 780 3.7 2.1 48 150 840 3.6 2.1 48 457 150 900 3.8 2.1 48 150 960 3.8 2.1 52 457 150 Feed $SO_2 = 516$ mg/1 1020 3.7 2.1 52 150 1080 3.5 2.1 48 441 150 1140 3.8 2.1 52 150 1200 3.6 2.1 52 457 150 Feed $SO_2 = 508 \text{ mg}/1$
1260 2.1 48 150 1260 2.1 48 150 1320 4.1 2.1 44 441 150 1380 4.2 2.1 40 150 1440

Table B-44. SO_2 oxidation column observations--11/11.

Figure B-27. SO₂ oxidation column observations.

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Figure B-28. SO₂ oxidation column observations.

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Table B-46. S02 oxidation column observations--11/16.

Figure B-29. SO₂ oxidation column observations.

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Table B-47. SO₂ oxidation column observations--11/17.

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*Start new feed tank

Table B-48. 802 oxidation column observations--ll/20.

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 $\label{eq:2.1} \frac{d\mathbf{r}}{d\mathbf{r}} = \frac{1}{2} \sum_{i=1}^n \mathbf{r}_i \mathbf{r}_i \mathbf{r}_i \mathbf{r}_i$

Note: Baekwashing:

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Run tap water up through column, 120 ℓ /hr for 20 min., monitor pH and time.

Column expanded 20% (5 em) Bed resettled only 2.5 cm, new bed depth = 27.5 cm

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Table B-49. S02 oxidation column observations--11/23.

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Figure B-30. SO₂ oxidation column observations.

Appendix C

Oxygen Reguirements

M. W. $SO_2 = 64$ **M.** $W. HSO_3 = 81$ **M. W.** $0_2 = 32$

500 mg/1 SO₂ ($\frac{81}{64}$) = 633 mg/1 HSO₃⁻ At pH 2.5, all aqueous ${50}$ is in $H{50}$ ⁻ form $HSO_3^- + \frac{1}{2}O_2 \rightarrow SO_4^ 0_2$ required = 633 ($\frac{16}{81}$) = 125 mg/1 Air flow for 150 ml/min.: Assume: Air = 21% O₂ $1 \t{2}$ air = 1.06 g 8% air to water oxygen transfer efficiency 125 mg/l x 0.00015 x 10^6 ml/min. x 1 g/ml = 0.01875 g 0_2 /min. 0.01875 g O₂/min. x 1/0.21 x 1 $\ell/1.06$ g air x 1/0.08 x 60 min./h = 63 ℓ/hr

Appendix D

Cost Data

Assumptions for estimating costs of filters

1) Use EPA cost curves for dual media filters.

(EPA 1980, Innovative and Alternative Technology Assessment Manual)

- 2) Use ENR cost index 3357 (November 1980).
- 3) To enter EPA construction cost curves, multiply flows by 4 for worst case and by 2 for best case to account for different filter loading rates.
- 4) Add cost of activated carbon media; ignore cost of sand and anthracite (used to make up cost of influent feed modifications).
- 5) Carbon cost equal for best and worst case.
- 6) Add cost to epoxy line concrete structures.
- 7) Add cost of forced draft blowers.

Activated carbon requirements

- $-$ Assume: 0.046 lbs/gal (5.5 g/1)
- Mass Required per MGD = 46,000 lbs
- $-A.C.$ Cost = $$0.83/1b$, FOB Kentucky

Use \$1.085/lb Installed

FILTRATION, DUAL MEDIA FACT SHEET 3.1.7

Description - Dual media filtration-gravity is one of the most economical forms of granular media filtration. Granular media filtration involves the passage of water through a bed of filter media with resulting deposition of solids. Eventually, the pressure across the bed becomes excessive or the ability of the bed to remove suspended solids is impaired. Cleaning is then necessary to restore operating head and effluent quality. The time in service between cleanings is termed the run length. The head loss at which filtration is interrupted for cleaning is called the terminal head loss, and this head loss is maximized by the judicious choice of media **sizes.**

Dual media filtration involves the use of both sand and anthracite as filter media. with anthracite being placed on top of the sand. Gravity filters operate by either using the available head trom the previous treatment unit. or by pumping to a flow split box after which the wastewater flows by gravity to the filter cells. Pressure filters utilize pumping to increase the available head.

Normally filter systems include multiple filter compartments. This allows for the filtration system to continue to operate while One compartment is being backwashed.

A filter unit generally consists of a containing vessel, the filter media, structures to support the media, distribution and collection devices for influent. effluent and backwash water flows. supplemental cleaning devices (see "Common Modifications"), and necessary controls for flows, water levels and backwash sequencing.

Common Modifications - Filtration systems can be constructed out of concrete or steel. with single or multiple compartment units. Steel units Can be either horizontal or vertical and are generally used for pressure filters. Systems can be manually or automatically operated.

Backwash sequences can include air scour or surface wash steps. Backwash water can be stored separately or in chambers that are integral parts of the filter unit. Backwash water can be pumped through the unit or can be supplied through gravity head tanks.

Technology Status - Has been used for many years in the potable water industry, and has been used in the wastewater treatment field for 10 to 15 years.

Typical Equipment/No. of Mfrs. (23) - Dual media filters/20; blowers/7; controls/29.

Applications - Removal of residual biological floc in settled effluents from secondary treatment and removal of residual chemical-biological floc after alum. iron. or lime precipitation in tertiary or independent physicalchemical waste treatment.

In these applications filtration may serve both as an intermediate process to prepare wastewater for further treatment (such as carbon adsorption. clinoptilolite ammonia exchange columns. or reverse osmosis) or as a final polishing step following other processes.

Limitations - Economics are highly dependent on consistent pretreatment quality and flow modulations. Increasing suspended solids loading will reduce run lengths, and large flow variations will deleteriously effect effluent quality in chemical treatment sequences.

Performance -

Chemicals Required - Alum and iron salts. and polymers can be added as coagulant aids directly ahead of filtration units. This. however. will generally reduce run lengths.

Residuals Generated - Backwash water, which generally approximates two to ten percent of the throughput. Backwash water can be returned to the head of the plant.

wash rate head loss 6 to 15 ft. teria (99) -
-rate 2 to 8 gal/min/ft ²; bed depth 24 to 48 inches (depth ratios of 1:1-4:1 sand to anthracite); back-
15 to 25 gal/min/ft ; air scour rate 3 to 5 stdft /min/ft ; filter run length 8 to 48 hours; terminal

Unit Process Reliability- Dual media filtration systems are very reliable from both a process and unit standpoint.

Environmental Impact - Requires relatively little use of land. Backwash water will need further treatment, with an ultimate production of solids which will need disposal. Air scour blowers usually need silencers to control noise. No air pollution generated.

Referenco~ - 2J: **26, 39, 44, 99**

Corrosion lining costs, worst case

For 1 MGD, Assume two filters, 23' sq x **6'** deep, ea Total wall area = $(23 \times 6) \times 8 = 1104 \text{ ft}^2$ Total floor area = $(23 \times 23) \times 2 = \frac{1058}{2162}$ ft² For 10 MGD, Assume four filters, 74' sq x **6'** deep, ea Total wall area = $(74 \times 6) \times 16 = 7104$ Total floor area = $(74 \times 74) \times 4 = 21904$ Total = 29000 sq ft Lining costs, use \$10/SF

Double costs to account for lining backwash storage tank

Corrosion lining costs, best case

For 1 MGD, Assume two filters, 14' sq x 10' deep, ea Total wall area = $(14 \times 10) \times 8 = 1120 \text{ ft}^2$ Total floor area = $(14 \times 14) \times 2 = \frac{392}{1512}$ ft² For 10 MGD, Assume four filters, 30' sq x 10' deep, ea Total wall area = $(30 \times 10) \times 16 = 4800$ Total floor area = $(30 \times 30) \times 4 = 3600$ Total = $\frac{3000}{8400}$ ft² Lining costs, use \$5/SF Double costs to include backwash storage tank

1) Horsepower requirements for blowers

Headloss through activated carbon by air

*Assume underdrain headloss = 2 x media H_L

2) Annual power cost for blowers

*Assume: 90% motor eff.

85% power factor

 \therefore 1 HP \cong 1 kw

** 24 hrs/day, 365 days/yr

		Best Case		Worst Case	
	Unit	1 MGD $(\hat{\mathbf{s}})$	10 MGD $($ \$)	1 MGD $(\hat{\mathbf{s}})$	10 MGD (5)
1.	SO ₂ Equipment including installation	20,000	20,000	20,000	20,000
2.	Absorption Tower complete w/fan Equipment a. Installation b.	22,983 4,596	190,561 38,112	28,728 11,491	236,551 94,620
3.	Contact Basin (30 min) Materials including a_{\bullet} lining Installation, Ъ. miscellaneous	16,169 4,850	150,080 45,024	30,518 15,259	281,960 140,980
4.	Pumps Absorption tower a. pump	3,000	3,000	3,000	3,000
5.	Oxidation Process, complete	687,100	3,352,600	1,065,200	5,393,200
6.	Lime Process Equipment a. Installation Ъ.	46,250 9,250	73,550 14,710	75,050 37,525	84,050 42,025
SUBTOTAL			$$814, 198 \mid $3,887,637 \mid $1,286,771 \mid $6,296,386$		
7.	Electrical & Piping	162,840	777,527	312,693	1,574,096
TOTAL CAPITAL**			\$997,000 \$4,665,000 \$1,608,000 \$7,870,000		

Table D-l. Summary of capital costs for sulfur dioxide disinfection systems. *

*Nielsen, Maxwell & Wangsgard-Montgomery. 1981. Preliminary report for sulfur dioxide disinfection pilot plant. ** Values rounded to nearest $$1,000$.

Item	Best Case		Worst Case		
	1 MGD $(\$)$	10 MGD $(\hat{\theta})$	1 MGD $($ \$)	10 MGD $($ \$ $)$	
Chemicals	15,464	154,640	57,904	579,040	
Power	7,457	81,936	12,752	134,857	
Maintenance	3,049	12,841	8,309	33,869	
Labor	3,300	4,620	5,665	25,800	
Σ ΟδΜ	\$29,270	\$254,037	\$84,630	\$773,566	

Table D-2. Summary of O&M costs for sulfur dioxide disinfection systems excluding $SO₂$ oxidation.