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SOURCES AND FATE OF TRS COMPOUNDS IN A PULP MILL ASB

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ABSTRACT

The source and treatability of TRS emissions at a mill in the Southeastern USA was studied in connection with potential capital upgrades in response to recently promulgated regulations. The front-end of the lagoon is anaerobic, and is associated with odor, which drops markedly beyond the aerated zone. Laboratory work with wastewater from two mills showed that the rate of H₂S degradation corresponded to that of oxygen consumption, confirming that the two processes were related. The rates were biphasic; the initial decrease was rapid, and then a slower process took over. The rate of the slower process equaled the degradation rate of H₂S in distilled water, suggesting that it originated from the uncatalyzed oxidation of H₂S. Hence, H₂S oxidation appears to be initially catalyzed by a wastewater component that is inactivated before the process goes to completion. Subsequent degradation of H₂S then occurs through the uncatalyzed step. Wastewater taken from the lagoon showed the presence of the transition metals necessary for sulfide catalysis. A dissolved oxygen level of 1 ppm was sufficient to suppress H₂S formation, and the lagoon was modeled in order to add an optimum level of aeration.

KEYWORDS

Biphasic; catalysis; oxidation; rate; TRS.

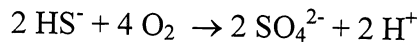
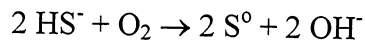
INTRODUCTION

A bleached kraft mill in the Southeastern USA encountered odor issues from the wastewater treatment system. Potential changes in the treatment system were being contemplated as part of a program to comply with the "cluster rules" recently promulgated in the USA. One option for the mill was to "hard-pipe" the condensate to secondary treatment, but this would add TRS compounds to the system. In order to evaluate odor issues, we studied the source and fate of TRS compounds in both laboratory and field work.

Oxygen reacts with sulfide quite slowly, and the two can even coexist for long periods in the presence of inhibitors (Chen and Morris, 1972). On the other hand, metals and organic constituents of wastewater can catalyze oxidation. Buisman et al. (1990) found that the biological oxidation of sulfide with oxygen at pH 8 can be 75 times faster than the corresponding rate of uncatalyzed chemical oxidation at sulfide concentrations of up to 10 mg/L, and about sixfold faster at sulfide concentrations of up to 600 mg/L. Fox and Venkatasubbiah (1996) cultured sulfide-oxidizing organisms from municipal sewage, and effectively converted sulfide in anaerobic reactor effluent to elemental sulfur. Both aerobic and anaerobic bacteria are able to oxidize H₂S to

sulfur. A review by Kuhn et al. (1983) shows that air oxidation of sulfides can be catalyzed, with the catalytic activity of metal ions in solution at 5 ppm being ranked as Co = Ni > Mn > Cu = Fe. The catalytic effect of Co and Ni was proportional to catalyst concentration in the 0.5-5 ppm range.

The mechanisms of sulfur oxidation are not completely understood, probably because multiple oxidation states are available to sulfur species. The most reduced form of sulfur is H₂S, and the most oxidized form is SO₄²⁻, and it is difficult to predict the degree of oxidation. It appears from the article of Kuhn et al. (1983) that the nature of the end products is governed largely by the O₂:S²⁻ ratio, although pH is another important factor as pointed out by Chen and Morris (1972). Elemental sulfur and sulfate have frequently been reported as stable end products of sulfide oxidation. Sulfide speciation depends upon the pH of the solution, and Hoffman (1977) showed that HS⁻ is the principal reactive species. The two most important bioconversions in an aerobic sulfide removal system are (Buisman et al., 1991; Janssen et al., 1997):



The following rate law is usually proposed for sulfide oxidation: $R_i = k[S]^a [O]^b$

Jolly and Forster (1985) reported a value of 1.15 for 'a' and 0.69 for 'b'. Wilmot et al. (1988) found 'a' and 'b' to be 0.38, and 0.21, respectively. Buisman et al. (1990) proposed 0.41 for 'a' and b = n log [S], where n = 0.39. O'Brien and Birkner (1977) reported 'a' and 'b' values of 1.02 and 0.8, respectively. The variability of 'a' and 'b' reflects the multiplicity of available pathways.

LABORATORY STUDIES OF SULFIDE OXIDATION IN WASTEWATER

Wastewater was collected from the influent of the mill of principal interest (mill A), and also from that of a second Southeastern mill (mill B) on November 25, 1997, and March 18, 1998, respectively. Their characteristics are listed in Table 1. The water was filtered (0.45μ), and spiked with sodium sulfide, whose depletion was monitored with a sulfide-specific electrode. Measurements were made at pH 7.5, and at 1.25 mg/L dissolved oxygen (DO). As shown in Figure 1, the initial disappearance of sulfide was much faster in wastewater than in deionized (DI) water, suggesting the presence of a catalyst in the wastewater. Manganese and iron are known catalysts of the reaction, as discussed above; they are present in the wastewater (Table 1), and may be responsible for the catalytic activity. All three rates converged after about 5-10 minutes, possibly because of catalyst inactivation. In order to verify that the degradation of sulfide was primarily due to oxidation, oxygen depletion rates were measured in the presence of sulfide, as shown in Figure 2. Although the absolute rates are not comparable with those in Figure 1, since the concentrations of sulfide and DO are not the same, they are within a factor of about two of each other, confirming that they are both oxidation processes. The rate of DO depletion in wastewater from mill B was similar to that from mill A.

Table 1: Analytes in wastewater ¹				
element	mill A		mill B	
	total (mg/L)	filtered (mg/L)	total (mg/L)	filtered (mg/L)
Mn	0.39	0.353	1.41	1.39
Fe	1.44	1.17	0.557	0.423
Zn	0.130	0.0934	0.382	0.363
Al	7.57	5.65	1.31	1.12
Sr	0.173	0.168	0.401	0.396
Ba	0.0663	0.060	0.567	0.549
Na	489	485	333	331
Mg	6.22	5.92	7.12	7.02
Ca	44.3	42.3	95.8	94.4
COD	860	700	1060	970
TSS	64			
¹ elements present at below 0.1 ppm are not reported				

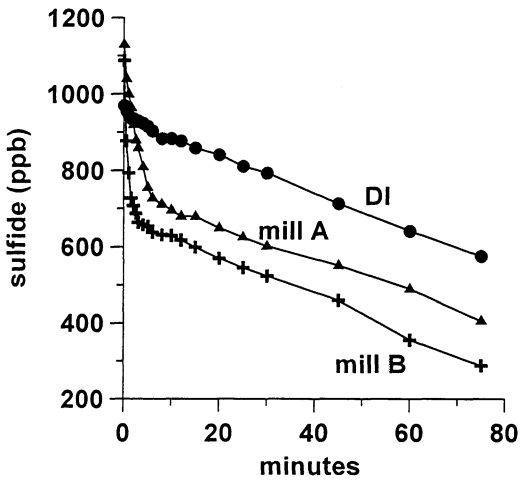


Figure 1: Sulfide removal in DI water and wastewater.

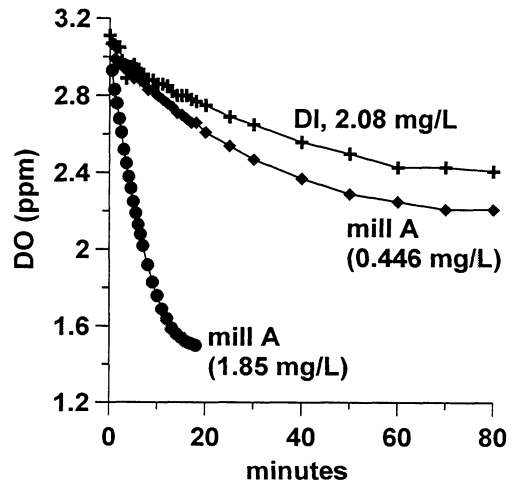


Figure 2: DO depletion in DI water and mill A wastewater at various sulfide levels.

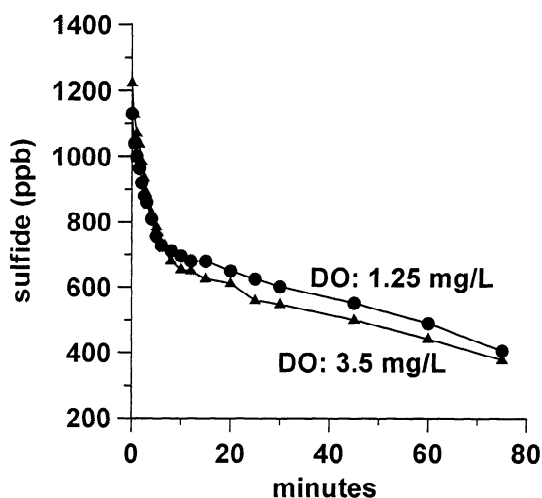


Figure 3: Effect of DO on sulfide degradation in mill A wastewater.

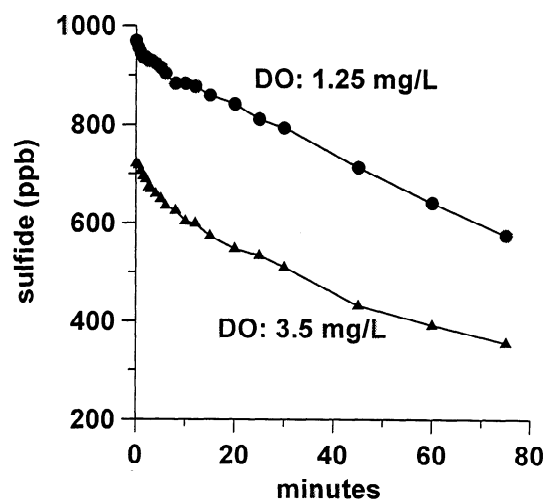


Figure 4: Effect of DO on sulfide degradation in DI water.

Since stripping rather than oxidation could be potentially responsible for some of the sulfide loss, we ran experiments at both pH 7.5 and 8.5 at a DO of 1.25 mg/L. The kinetics of sulfide decrease were nearly identical at the two pH values. H_2S has a pK_a of 7 (Hoffman 1977), which means that H_2S and HS^- are present in equal amounts at $\text{pH}=7$. Since H_2S is volatile, whereas HS^- is not, the loss of total sulfide would have been much faster at pH 7.5 than at a pH of 8.5, if stripping from water were important. Since the two rates were nearly identical, sulfide removal is almost entirely due to oxidation as opposed to stripping. However, since HS^- is the reactive species, and since the concentration of HS^- is much higher at pH 8.5 than at pH 7.5, one might have expected the rate to be faster at pH 8.5, which is clearly not the case. The behavior observed could result if a catalyst was involved, and if the surface of the catalyst was saturated. In other words, the catalyst can only process so many HS^- molecules at a time, beyond which the presence of additional sulfide would not affect the rate. The intermediacy of a catalyst is also implicated in Figures 3 and 4, which show the effect of DO on sulfide oxidation in mill A wastewater, and distilled water, respectively, at a pH of 7.5. DO makes no significant difference to the rate, which means that it is not involved in the rate-limiting step. In summary, sulfide is removed from the wastewater system primarily through oxidation. A wastewater component present in small quantities catalyzes the oxidation.

FIELD STUDIES

The secondary treatment system at mill A is illustrated in Figure 5, and the lagoon characteristics are listed in Table 2. Samples collected on November 25, 1997, were analyzed for various components, and the results are tabulated in Table 3. For the dissolved sulfide measurements, the solids were flocculated by the addition of aluminum chloride, and measurements made on the supernatant. The total sulfide in Table 3 refers to both dissolved and bound sulfide. For these

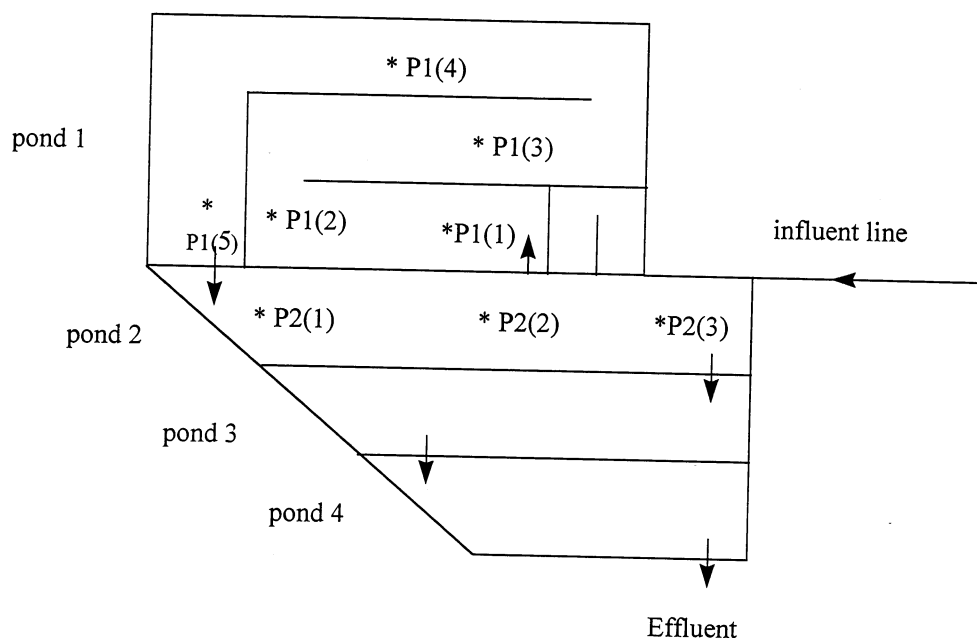


Figure 5: Schematic of the secondary treatment system at mill A

Table 2: Lagoon characteristics at mill A				
pond #	area (m²)	depth (m)	volume (m³)	total horse-power
1	1.963×10^6	1.067	2.094×10^6	0
2	7.085×10^5	1.22	8.644×10^5	240
3	5.384×10^5	1.13	6.084×10^5	480
4	3.805×10^5	1.22	4.642×10^5	0

measurements, the sample was preserved with zinc acetate which forms zinc sulfide. Excess iodine was added, and the residual iodine determined titrimetrically. Note that the sulfide increases along ponds 1 and 2, and declines thereafter, indicating that the sulfide is generated biologically. Also, bound sulfide exceeds free sulfide by a wide margin. Since the bound sulfide does *not* correlate with TSS, it is probable that the sulfide binds to colloidal material. There is a rough correlation between total sulfide and pH as shown in Figure 6, but this could merely reflect an increase in both pH and sulfide as pond 1 was traversed. As discussed earlier, sulfide volatility is high at $\text{pH} \leq 7$, and increasing the pH to beyond 7 should reduce odor. Figure 7 plots dissolved sulfide against DO, and is compelling in that sulfide concentrations rise sharply at $\text{DO} < 1$. Clearly, adding aeration should be effective for odor reduction.

Table 3: Total sulfide concentrations in the mill A treatment system.

location	total sulfide (ppm)	dissolved sulfide (ppb)	pH	DO (mg/L)	TSS (mg/L)
influent pond 1	5	85	6.38	0.99 ^c	64
P1(1)	7	167	6.82	0.46	32
P1(2)	18	353	6.89	0.33	28
P1(3)	12	317	7.40	0.34	36
P1(4)	16	257	7.65	0.21	108
P1(5)	32	188	7.90	0.46	24
influent pond 2	19	188	7.85	0.48	6
P2(1)		193	7.82	0.38	14
P2(2)		195	7.56	0.58	14
P2(3) ¹	21	168	7.48	0.35	26
effluent pond 2 ²	3	90	7.50	3.52	
influent pond 3	3	90	7.54	3.29	32
P3(1)					24
P3(3)					18
P3(5)					12
influent pond 4	2	68	7.50	6.00	22
effluent pond 4	3	47	7.50	1.90	20

¹ non-aerated zone; ² aerated zone; ³ aerated during sample collection

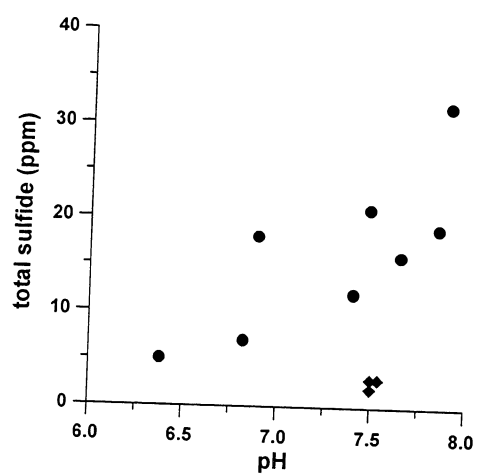


Figure 6: Relationship between total sulfide and pH (●: ponds 1,2; ◆: ponds 3,4)

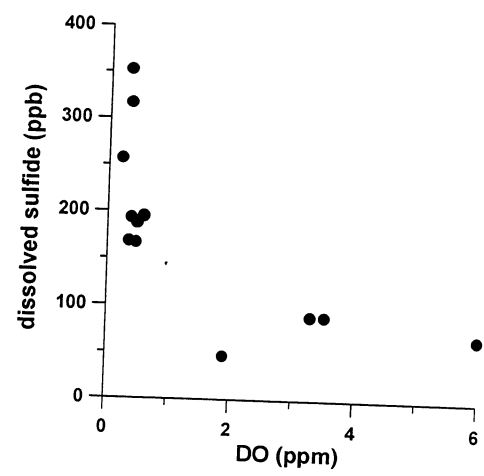


Figure 7: Relationship between dissolved sulfide and DO

In conclusion, H₂S is generated anaerobically in ponds 1 and 2. Much of the sulfide is bound by colloidal wastewater components, and the small remaining fraction is responsible for the odor. Oxidation of this fraction is catalyzed by wastewater components, and is *potentially* rapid, unless the catalyst is saturated. However, the laboratory work showed that about 550 ppb of sulfide can be rapidly removed, and the dissolved sulfide levels in Table 3 are much lower. Inhibiting biological production of H₂S by raising the DO to 1 mg/L or more should be the most effective means of odor reduction.

Field data acquired at mill A during February 1998 shows a 100 ppm reduction in sulfate concentration across pond 1. The corresponding drop across pond 2 is only about 10 ppm, and there is little or no decrease in ponds 3 and 4. The decrease amounts to about 1,000 lb/hour of sulfate, which corresponds to 333 lb/hour of sulfur. Since much of the sulfate will convert to sulfide under the anaerobic conditions prevailing in ponds 1 and 2, the additional 45 lb/hour of TRS that could originate from hardpiping the condensate represents a small additional load, especially in view of the fact that this analysis represents a *worst-case* scenario.

SUMMARY

- H₂S degrades much faster in wastewater than in distilled water.
- At pH > 7, much more H₂S is lost through oxidation than through stripping.
- Twenty five thousand pounds of sulfate are lost per day across ponds 1 and 2, and cannot presently be accounted for. Sulfide concentration increases along ponds 1 and 2, and declines thereafter, indicating that some of the sulfate converts to H₂S.
- Current TRS emissions (most of which is H₂S) are estimated to be < 1,000 lb/hr. Bound sulfide levels greatly exceed those of free sulfide.
- Sulfide levels rise sharply at DO < 1 ppm. DO levels of ≥1 ppm can be maintained if ponds 1-3 carry the following levels of aeration. Pond 1: 520 hp; pond 2: 315 hp; pond 3: 125 hp.
- H₂S generation in pond 1 can be essentially eliminated by adding aerators.

REFERENCES

- Buisman C. J. N., Ijspeert P., Janssen A. and Lettinga G. (1990). Kinetics of chemical and biological sulphide oxidation in aqueous solutions. *Wat. Res.*, **24**(5) 667-671.
- Buisman C. J. N., Ijspeert P., Hof A., Janssen A. J. H., ten Hagen, R. and Lettinga, G. (1991). Kinetic parameters of a mixed culture oxidizing sulfide and sulfur with oxygen. *Biotechnol. Bioeng.*, **38**(8), 813-820.
- Chen K. Y. and Morris J. C. (1972). Oxidation of sulfide by O₂: catalysis and inhibition. *Journal of the Sanitary Engineering Division*, Proceedings of the ASCE, **98**(SA1), 215-227.
- Fox P. and Venkatasubbiah V. (1996). Coupled anaerobic/aerobic treatment of high-sulfate waste-water with sulfate reduction and biological sulfide oxidation. *Wat. Sci. Tech.*, **34**(5-6), 359-366.
- Hoffman M. R. (1977). Kinetics and mechanism of oxidation of hydrogen sulfide by hydrogen peroxide in acidic solution. *Environ. Sci. Technol.*, **11**(1), 61-66.
- Janssen A. J. H., Ma S. C., Lens P. and Lettinga G. (1997). Performance of a sulfide-oxidizing expanded-bed reactor supplied with dissolved oxygen *Biotechnol. Bioeng.*, **53**(1), 32-40.
- Jolley R. A. and Forster C. F. (1985). The kinetics of sulphide oxidation. *Environ. Technol. Letters*, **6**, 1-10.
- Kuhn A. T., Kelsall G. H. and Chana M. S. (1983). A review of the air oxidation of aqueous sulphide solutions. *J. Chem. Technol. Biotechnol.*, **33A**, 406-414.
- O'Brien D. J. and Birkner F. B. (1977). Kinetics of oxidation of reduced sulfur species in aqueous solution. *Environ. Sci. Technol.*, **11**(12), 1114-1120.
- Wilmot P. D., Cadee K. and Katinic J. J. (1988). Kinetics of sulfide oxidation by dissolved oxygen. *J. Water Pollution Control Federation*, **60**, 1264-1270.

