

Management of hydrogen sulphide generation at a Kraft mill effluent plant

E Rava^{1*}, JJ Schoeman¹, PJ Allison² and V Dilsook³

¹ University of Pretoria, Department of Chemical Engineering, Water Utilisation Division, 0002, South Africa

² Buckman Laboratories (Pty) Ltd, PO Box 591, Hammarsdale, KwaZulu-Natal, 3700, South Africa

³ Sappi Management Services - Technology Centre, PO Box 6, Pretoria, 0087, South Africa

Abstract

Communities surrounding an integrated Kraft mill noticed odours from the mill's effluent treatment plant. A project was therefore commissioned by the mill to proactively manage the odours from both the pulp-processing operations and the effluent treatment plant. This project formed part of a co-ordinated study that was implemented by the mill to limit emissions of the total reduced sulphur (TRS) components from the pulp mill operations. It was found that sulphate-reducing bacteria (SRB) converted the sulphates present in the effluent to hydrogen sulphide (H₂S) by dissimilatory respiration. The combined use of a nitrate-releasing biomodifier (Bulab® 9518) and an anthraquinone sulphate-reduction inhibitor (Busperse® 2432) was effective in reducing both SRB activity and H₂S levels. The average aqueous H₂S levels (40 mg/l) were reduced to between 92% and 99%.

Keywords: biomodifiers, hydrogen sulphide, Kraft mill effluent plant, sulphate-reducing bacteria (SRB), anthraquinone, sulphate reduction inhibition, sodium nitrate

Introduction

The typical odours associated with Kraft mills are due to the generation of four reduced sulphur gases such as hydrogen sulphide (H₂S), methyl-mercaptan (CH₃SH), dimethyl-sulphide (CH₃)₂S and dimethyl-disulphide (CH₃)₂S₂. These gases are collectively referred to as total reduced sulphur (TRS) components (Bonnin, et al., 1990; Pinkerton, 1999; Olendorf et al., 2000; Bordado et al., 2003).

The potential point sources of emissions include the Kraft recovery furnaces, smelt dissolving tanks, lime kilns, brown stock washers, digesters, evaporators, condensate strippers, black liquor oxidation systems, tall oil recovery systems, liquor storage tanks and condensate strippers (Gellman, 1972; Hagen et al., 1997; Pinkerton, 1999; O'Connor et al., 2000). The potential diffuse source emissions include the clarifiers, thickeners, wastewater treatment systems and on-site landfills (Collela et al., 1992; O'Connor et al., 2000; Bordado et al., 2003).

The sulphate-reducing bacteria (SRB) are a diverse group of bacteria characterised by their anaerobic nature (O'Faherty et al., 1995; Kosinska et al., 2005) and their ability to use oxidised sulphur compounds such as sulphur (S⁰), thiosulphate (S₂O₄), sulphite (SO₃⁻²) or sulphate (SO₄⁻²) as terminal electron acceptors (Postgate 1984; Balows et al., 1992) for the dissimilation of organic material (Lukanich, 1995). The anion of choice is sulphate (Ballinger et al., 2001) which has the highest sulphur oxidation state (+6) (Atlas et al., 1993; Barbosa et al., 2004) and makes it a very stable compound with a low redox potential (Matias et al., 2005).

Desulphovibrio are the most common SRB genera found in paper mills (Korhonen et al., 1978) and wastewater (Lukanich, 1995; O'Flaherty et al., 1995). They have a relatively high sulphate reduction rate (Gaylarde, 1992) and their growth rate is affected by the availability of an organic carbon source, inorganic sulphates, pH, temperature, salinity, (Kosinska et al., 2005), COD/SO₄ ratio (Polanco et al., 2001; Kosinska et al., 2005) and redox potential (Czechowski et al., 1981; Postgate, 1984).

SRB can tolerate pH environments of between 4 and 10 and temperatures ranging between 35° and 55°C (Korhonen et al., 1978). The enzyme activity is most stable between pH 5.8 and pH 8.4 and temperatures between 40°C and 42°C (Czechowski et al., 1980). They conduct their main metabolic oxidations within a redox span around an oxidation-reduction potential (ORP) of -150 mV to -200 mV. Their growth is accompanied by a drop in redox potential to the -250 mV range.

Use of biomodifiers to manage H₂S levels

In the absence of dissolved oxygen, nitrates (Norwood et al., 2001; Bratcova et al., 2002; Greene et al., 2003) can act as alternative electron acceptors to a group of facultative aerobic denitrifying bacteria (denitrifiers) (Norwood et al., 2001). This will result in a population shift which suppresses SRB anaerobic activity (Bentzen et al., 1995; O'Flaherty et al., 1995) due to an increase in the redox potential (> -200 mV) of the environment (Ballinger et al., 2001). The denitrifiers out-compete the SRB for the available nutrients due to their thermodynamic and physiological properties (Hitzman et al., 1998).

The microbial competition for the organic carbon increases when decreasing the COD/SO₄ ratio (Polanco et al., 2001). The SRB are eventually left without sufficient carbon source and thus their growth and activity are inhibited (Ballinger et al., 2001; Groleau et al., 2002) and H₂S is not produced (Hitzman et al., 1998) due to the suppression of sulphate reduction (Seitz et al., 1986).

* To whom all correspondence should be addressed.
Current address: Buckman Laboratories (Pty) Ltd, PO Box 251, Bedfordview 2008, South Africa.
☎ +27 11 997-5100; fax: +27 11 455-4495;
e-mail: emrava@buckman.com
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Use of sulphate reduction inhibitors to manage H₂S levels

Antraquinones (AQ) have specific mechanisms which compete with the sulphate ion for the active site on the adenosine triphosphate (ATP) sulphurylase enzyme. This results in the formation of an unstable analogue complex which easily hydrolyses to adenosine monophosphate (AMP). The sulphate analogue is then available again to react with the ATP sulphurylase enzyme (Weimer et al., 1995; Lie et al., 1999). The repetition of this reaction with the analogue results in the depletion of ATP in the cell, thus reducing the energy available for sulphate activation which eventually results in the inhibition of SRB growth (Cooling et al. 1996; Ballinger et al. 2001).

Experimental

Grab samples (1 000 mℓ) were taken weekly, over a 7-month period, at the effluent sump post clarification (solids removal). Test samples were prepared on site for SRB activity/H₂S generation studies by filling 100 mℓ sterile glass bottles with effluent to which Bulab® 9518 and Busperse® 2432 were added at concentrations based on studies published by Howe et al. (1967), Mouche et al. (1987), Hunniford et al. (1990), Hitzman et al. (1995), Craig et al. (1996), Hitzman et al. (1998) and Norwood et al. (2001). The test bottles were tightly closed, shaken and incubated at 50°C to simulate the conditions at the effluent treatment plant. Untreated samples were used as the control samples. SRB activity was quantified using modified iron sulphite agar (Mara and Williams 1970; Postgate, 1984) and enumerated according to procedures published by De Bruyn et al. (1992), Tatnall et al., (1998) and Harless (2000). The pH, chemical oxygen demand (COD), hydrogen sulphide (H₂S), dissolved oxygen (DO) and temperature of the samples were determined on site and then preserved according to standard procedures. Samples were further analysed for inorganic constituents by the laboratories of the CSIR (Pretoria, South Africa).

Results and discussion

The composition of the untreated effluent is shown in Table 1.

The results presented in Table 1 indicated that the effluent provided a suitable environment for SRB activity and the generation of aqueous H₂S by dissimilatory reduction of sulphate because of the following:

- Relatively high SRB population was present
- An organic carbon source (Lukanich, 1995, O'Flaherty et al., 1995) was available in the form of COD (Kim et al., 2003)
- An electron acceptor was available in the form of inorganic sulphate (Postgate 1984; Balows et al., 1992, Ballinger et al., 2001)
- Anaerobic conditions were present due to low dissolved oxygen levels (< 1 mg/ℓ) (Howe et al, 1967; Ballinger et al., 2001)
- Molybdenum was available for the production of SRB enzymes and co-factors (Chen et al., 1998)
- Temperature and pH were within the ranges reported by Korhonen et al., (1978)
- Salinity was available in the form of sodium (Kosinska et al., 2005)
- o-Phosphate was available as a micro-nutrient for SRB activity (Ballinger et al., 2001; Kosinska et al., 2005)
- Iron and manganese catalysed the generation of H₂S by SRB (Matsumura et al., 1992)
- High sulphate (Janssen et al., 1999) and low nitrate levels were typical of Kraft mill effluents (Norwood et al., 2001).

Treatment Option 1: Addition of Bulab® 9518

Bulab® 9518 (biomodifier) was slug-dosed to induce a population shift from the anaerobic SRB (Marschall et al., 1993; Bentzen et al., 1995) to the more aerobic denitrifying organisms (Hitzman et al., 1995). After an incubation period of 72 h at 50°C, a decrease in H₂S levels, increase in oxidation-reduction potential

TABLE1
Untreated effluent composition

Analysis	Detection limits	Minimum	Maximum	Average
Calcium (mg/ℓ as Ca)	0.1 ⁽¹⁾	8.80	132	62
COD (mg/ℓ as O ₂)	100 ⁽²⁾	1 250	6 390	2 920
Conductivity (μS/cm)	100 ⁽³⁾	2 360	4 230	3 030
Dissolved oxygen (mg/ℓ as O ₂)	0.2 ⁽³⁾	0.4	2.8	0.7
Hydrogen sulphide (mg/ℓ as H ₂ S)	1 ⁽²⁾	<1	310	40
Iron (mg/ℓ as Fe)	0.05 ⁽¹⁾	0.7	1.8	1.3
Manganese (mg/ℓ as Mn)	0.03 ⁽¹⁾	0.8	7.2	3.8
Molybdenum (mg/ℓ as Mo)	0.5 ⁽²⁾	<0.5	<0.5	<0.5
Nitrates (mg/ℓ as NO ₃)	0.1 ⁽²⁾	3.6	43	0.6
o-Phosphate (mg/ℓ as PO ₄)	0.1 ⁽²⁾	0.5	2.8	1.4
ORP (mV)	-	-300	-50	-116
pH	-	6.04	10.3	7.29
Salinity (mg/ℓ as Na)	0.3 ⁽¹⁾	223	925	521
SRB (cfu/ml)	10 ⁽⁴⁾	<10	940 000	2 200
Sulphates (mg/ℓ as SO ₄)	10 ⁽²⁾	310	724	522
Temperature (°C)	-	40	53	49

Number of samples tested: 25

⁽¹⁾ Atomic absorption spectrophotometry (AAS); ⁽²⁾ Colorimetric procedures;

⁽³⁾ Respective probes and instrumentation; ⁽⁴⁾ Iron sulphite agar

(ORP) and increase in pH was measured indicating that a population shift had most probably taken place (Table 2).

Bulab® 9518 (mg/ℓ)	ORP (mV)	pH	H ₂ S (mg/ℓ)	H ₂ S reduction (%)
Control	-300	6.69	8.5	0
25	-136	7.56	4.2	51
50	-131	7.89	4.2	51
100	-106	8.32	2.8	67
150	-70	8.44	2.2	78
200	-64	8.44	1.9	78
500	-60	8.54	1.8	79

The changes were most probably due to a number of biochemical processes having taken place:

- Nitrates used as an alternative electron acceptor (Seitz et al., 1986; Mouchè et al., 1987; Marschall et al., 1993) by SRB and denitrifying bacteria (Ballinger et al., 2001)
- pH increased due to the release of ammonia from amine-containing compounds (Birnbaum et al., 1984)
- pH increased due to the formation of hydrocarbonate ions generated during dissimilatory sulphate reduction in the presence of nitrate (Bratcova et al., 2002)
- Nitrates reduced to N₂ gas by denitrifiers when the COD/NO₃-N ratios were high (Polanco et al., 2001, Craig et al., 2001)
- ORP increased (Ballinger et al., 2001) due to the build-up of N₂ gas (Ballinger et al., 2001) which suppressed sulphate reduction (Bentzen et al., 1995; O'Flaherty et al., 1995)
- Denitrifiers used the pre-formed H₂S as a nutrient thus increasing the reduction of H₂S levels (Hitzman et al., 1995; Hitzman et al., 1998)
- Denitrifiers used H₂S as an electron donor when the dissolved oxygen levels were below 1 mg/ℓ (Polanco et al., 2001)
- Denitrifiers out-competed SRB for the available organic carbon source (Hitzman et al., 1995; Hitzman et al., 1998, Ballinger et al., 2001) due to the decrease in COD/SO₄ ratio (Polanco et al., 2001).

Treatment Option 2: Addition of Bulab® 9518 and Busperse® 2432

Bulab® 9518 (biomodifier) was slug-dosed to provide an alternative electron acceptor and Busperse® 2432 (AQ) was slug-dosed to inhibit SRB dissimilatory respiration and thus the reduction of sulphates to aqueous H₂S (Table 3).

Bulab® 9518: Busperse® 2432	Initial H ₂ S (mg/ℓ)	Final H ₂ S (mg/ℓ)	% Reduction
25:2	14	<1	99
50:4	50	4	92
100:8	200	60	70
100:8	310	160	48

Dosing of 50 mg/ℓ Bulab® 9518 and 4 mg/ℓ Busperse® 2432 into the clarified effluent sump would be sufficient to reduce the average aqueous H₂S level (40 mg/ℓ) by at least 92%. Higher product

dosages would be required as the aqueous H₂S levels increased.

The advantages of dosing Bulab® 9518 together with Busperse® 2432 were as follows:

- Lower dosages required due to the synergism between Bulab® 9518 and Busperse® 2432
- Cost-effective chemical treatment
- SRB specific and effective in anaerobic conditions
- Effective over a wide pH range.

Conclusions

The chemical results indicated that the composition of the untreated effluent was typical of Kraft mills and that it was suitable for the rapid growth of SRB. The effluent contained high levels of SRB, organics, sulphates, micro-nutrients and low levels of nitrate and nitrites. These conditions were favourable for the reduction of sulphates to aqueous H₂S by SRB dissimilatory respiration.

Option 1: The addition of Bulab® 9518 resulted in a population shift where denitrifiers most probably out-competed SRB for the available organic carbon source and nutrients making the effluent conditions more aerobic. The more aerobic conditions inhibited SRB activity which in turn increased the effluent pH, ORP and reduced the aqueous H₂S levels by 79%.

Higher Bulab® 9518 (>500 mg/ℓ) dosages would be required to improve the reduction of aqueous H₂S levels above 79%. The increased dosages would increase the cost of the treatment programme and the accumulation of sodium and nitrates could have a negative impact on the soil properties (salinity absorption ratio (SAR), cation exchange capacity (CEC), nutrient availability) and environment (runoff/leaching) since the effluent is used for the irrigation of pastures.

Option 2: The addition of Bulab® 9518 together with Busperse® 2432 was cost effective since lower dosages were required due to the synergism between the two products. Slug-dosing 50 mg/ℓ Bulab® 9518 and 4 mg/ℓ Bulab® 2432 reduced the average aqueous H₂S (40 mg/ℓ) by 92%.

It was recommended to slug-dose 50 mg/ℓ Bulab® 9518 and 4 mg/ℓ Bulab® 2432 into the launder point between the clarifier and the effluent sump. The pH, COD, H₂S, SO₄ and temperature of the effluent would need to be monitored to adjust the dosages accordingly so that an aqueous H₂S level of < 1 mg/ℓ could be achieved and maintained.

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