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Controlling TRS emissions from dissolving-tank vent stacks

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ABSTRACT

H_2S emissions from the smelt dissolving tank were evaluated using thermodynamic equilibrium calculations. Shatter jets are the main source of emissions when stack concentrations before the scrubber exceed 50 ppm H_2S. These emissions can be reduced by using more efficient steam nozzles and lowering steam pressures. Green liquor can also be a source of H_2S emissions, but chemical equilibrium in the process environment limits emissions to 20–30 ppm. H_2S emissions can be controlled to below 20–30 ppm by using weak wash or green liquor in dissolving-tank scrubbers. Methyl mercaptan from foul condensates can also be controlled using this approach. Caustic or oxidized white liquor must be used as scrubbing solutions if lower TRS emissions are required. Scrubbing with water cannot control TRS emissions at these levels.

Application:

Mills can reduce emissions from the dissolving-tank vent stacks by lowering steam pressure to the shatter jets.

EMISSIONS OF TOTAL REDUCED sulfur (TRS) from dissolving-tank vent stacks often exceed permitted limits. The conventional approach to controlling TRS emissions is by end-of-pipe treatment, i.e., scrubbing the vent gases. However, TRS levels can also be controlled by reducing emissions at their source. The first step in implementing such a control strategy is to identify the sources of the emissions.

In this paper, we examine the sources of TRS emissions from the dissolving-tank area and define the relative importance of various TRS sources to overall emissions. We then present alternatives for reducing these TRS emissions and show the results obtained from their application in several mill trials.

TRS EMISSIONS FROM GREEN LIQUOR AND WEAK WASH

The molten smelt droplets that fall into the dissolving tank contain mainly Na_2CO_3 and Na_2S. These droplets are dissolved in weak wash to produce raw green liquor. Both green liquor and weak wash consist largely of dissolved sodium salts, including sodium hydrosulfide (NaHS), in water. Table I shows typical compositions of green liquor and weak wash.

In solution, NaHS is in equilibrium with Na_2S and H_2S as depicted in Eqs. 1–3:

$$H_2S(g) \rightleftharpoons H_2S(aq) \quad (1)$$

$$H_2S(aq) \rightleftharpoons HS^- + H^+ \quad (2)$$

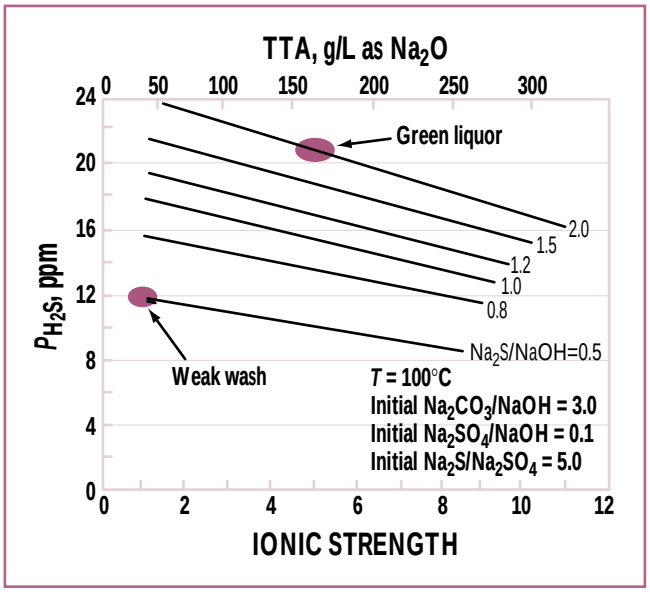
$$HS^- \rightleftharpoons S^{2-} + H^+ \quad (3)$$

The equilibrium constants for the reactions in Eqs. 1–3 at 100°C are given in Table II. In green liquor or weak wash, the sulfide species will be mainly S^{2-} and HS^-. However, these solutions have a finite $H_2S(aq)$ concentration and, according to Eq. 1, a small but finite equilibrium H_2S vapor pressure. Therefore, they can contribute to TRS emissions.

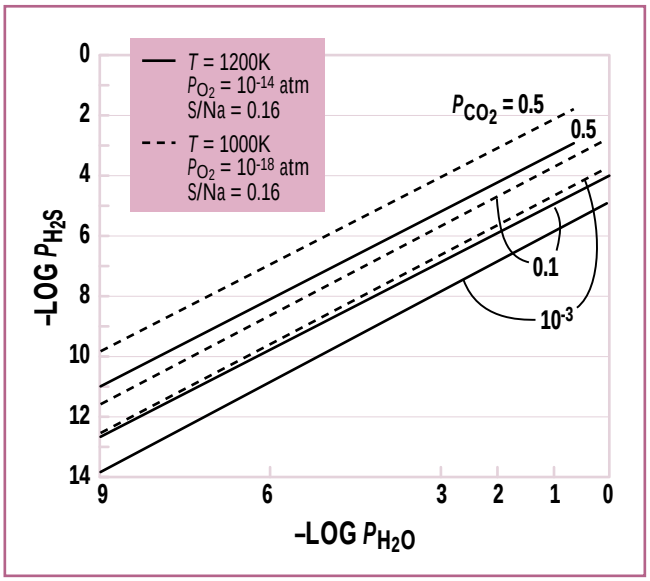
The equilibrium partial pressure of H_2S over green liquor and weak wash was estimated by considering the equilibria in Eqs. 1–3, parallel equations involving CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}, and the dissociation of water into H^+ and OH^-. Activity coefficients for the ionic species were estimated by Kusik and Meissner's method *(1)*. Details of the equilibrium calculations—including the equilibrium constants, activity coefficients, and the solution algorithm—are presented in detail by Danko *(2)*.

Figure 1 shows the calculated H_2S concentration in gases in equilibrium with alkaline aqueous solutions containing sulfide species. The regions representing the typical range for green liquor and weak wash are marked. These results show that higher H_2S emissions are to be expected from liquors with higher sulfidity and lower causticity, but that there would be relatively little effect of TTA (total titratable alkali) on H_2S emissions. The uncertainty for these H_2S values was calculated from the uncertainty in all of the thermodynamic data and activity coefficients that were used in the calculations. The main factor in the uncertainty was uncertainty in the activity coefficient data for sulfide species.

The results in Fig. 1 indicate that the H_2S emissions from the green liquor should not exceed 22±13 ppm. For weak wash, the H_2S emissions would be less, about 12±7 ppm. Experimental data to which the calculated results in Fig. 1 can be compared are very limited. Shih *et al. (3)* reported 10.5±1.4 ppm H_2S in the gas in equilibrium at 100°C with a buffer solution at pH 13 in which approximately 0.011 mole H_2S/mole NaOH had been dissolved. However, the data of Shih *et al.* was for an ionic strength of 0.04, and the pH for the buffer solutions was measured at



1. Partial pressure of H_2S (P_{H2S}) in gases in equilibrium with aqueous solutions of Na_2S and NaOH vs. TTA at 100°C. Ratios of sodium salts are mole ratios.



2. P_{H2S} as a function of P_{H2O} at three levels of P_{CO2} and two levels of temperature

25°C prior to addition of H_2S and heating to 100°C. Nevertheless, their data are in reasonable agreement with the data in Fig. 1.

The H_2S emissions of 20–30 ppm from the green liquor and the weak wash represent the maximum attainable if the liquids are well mixed with the dissolving-tank vent gases. The actual vent emissions from the liquor in the dissolving tank could be less.

TRS EMISSIONS FROM THE SHATTER JET

Smelt is another source of TRS emissions. To avoid dissolving-tank explosions, shatter jets, usually steam jets, are used to break up the stream of smelt exiting the recovery boiler into small droplets. Na_2S in smelt can react with water vapor and CO_2 to produce H_2S via the reactions in Eqs. 4 and 5:

$$Na_2S(l) + 2H_2O \rightleftharpoons H_2S(g) + 2NaOH \quad (4)$$

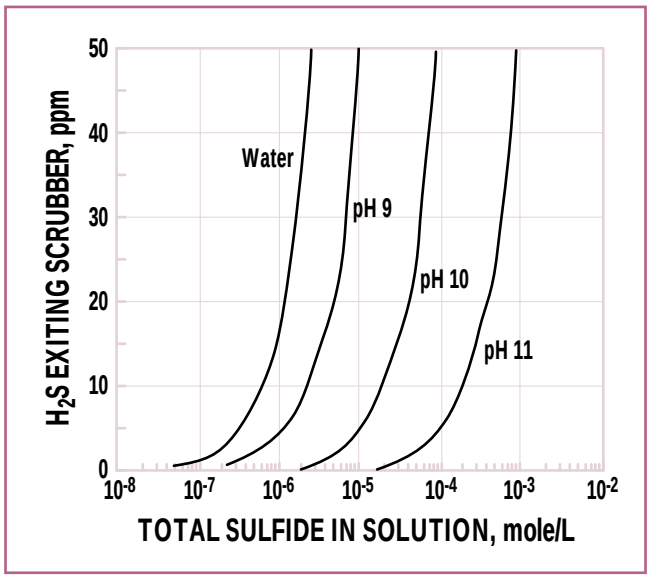
$$Na_2S(l) + H_2O + CO_2 \rightleftharpoons H_2S(g) + Na_2CO_3 \quad (5)$$

Equilibrium calculations were performed to estimate the maximum H_2S concentration in the gas phase that could result from shatter-jet operation. Equations 4 and 5, as well as the oxidation reactions for H_2S to SO_2 and Na_2S to Na_2SO_4, were included in the calculations. The smelt included Na_2S, Na_2CO_3, and Na_2SO_4. In some calculations, the smelt was assumed to contain NaOH as well, but this had little effect on the predicted H_2S emissions *(2)*. Activity coefficients for the smelt components were estimated using the regular solution method *(4)*. Details of the equilibrium calculations—including the equilibrium constants, activity coefficients, and the solution algorithm—are presented in detail by Danko *(2)*.

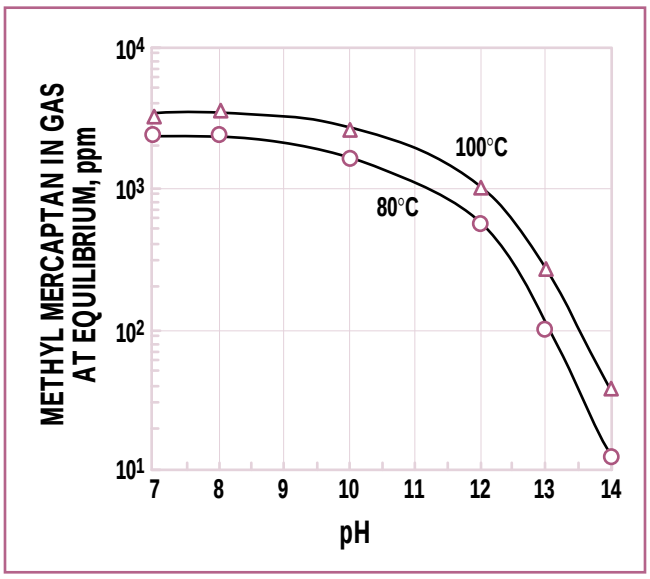
The equilibrium calculations were conducted such that the water vapor, O_2, and CO_2 contents of the bulk gas had to be specified. The dry-gas concentrations in Table III were measured at the shatter jets of a mill in Springfield, OR (Weyerhaeuser Co.).

Figure 2 presents the results of equilibrium calculations at 1000K and 1200K. The results show how the H_2S partial pressure depends on water vapor and CO_2 partial pressure at low O_2 partial pressure. Calculated results for two sets of specific conditions are included in Table IV. At 0.4% CO_2 and low oxygen concentrations, the H_2S concentration at equilibrium would be approximately 700 ppm at 1000K, and it would be higher at lower temperatures. At higher local CO_2 concentrations, the H_2S partial pressure at the shatter jets could approach 20,000 ppm.

Such high concentrations of H_2S would not be possible if the Na_2S in the smelt or the H_2S released from the smelt were being oxidized to Na_2SO_4 and SO_2. However, the conditions in the shatter-jet region are not conducive to oxidation. The concentration of water vapor at the shatter



3. Concentration of gaseous H_2S in equilibrium with total sulfide species in solution for pH 7–11 at 100°C



4. Concentration of gaseous methyl mercaptan in equilibrium with aqueous solutions for pH 7–14 at 80°C and 100°C. Total dissolved mercaptan concentration is 0.01 mole/L. Data are from Shih **et al. (6).**

KEYWORDS
Emission, furnaces, gas scrubbing, hydrogen sulfide, nozzles, pollution control, recovery furnaces, smelt dissolving tanks, steam, sulfides, sulfur compounds, tanks, total reduced sulfur.

jets is higher than that of O_2, and water vapor has a higher diffusivity than O_2. This means that water vapor will compete with O_2 to reach the surface of the smelt droplets and react with them. Moreover, H_2S would not react rapidly with O_2 at the gas temperatures near the shatter jets.

The TRS concentrations measured at the inlet to the dissolving-tank scrubber at the Springfield mill on two separate occasions were 50 ppm and 100 ppm. These levels are significantly higher than the H_2S concentration that would result if the vent gases were in equilibrium with the raw green liquor. The source of these higher TRS concentrations must therefore be the smelt shatter jets.

REDUCING TRS EMISSIONS FROM SHATTER JETS

H_2S emissions from the shatter-jet area can be reduced by decreasing the amount of steam used to shatter the smelt. This can be accomplished by installing more efficient shatter-jet nozzles and by lowering the pressure of the steam delivered to the shatter jets. At two mills in which the steam pressure at the shatter jets was reduced from 1030 kPa to 340 kPa (150 psig to 50 psig), TRS levels in the vent stack dropped by 33% and 20%. Neither mill encountered problems with smelt shattering at the lower steam pressure.

REMOVING TRS IN DISSOLVING-TANK VENT SCRUBBERS

Effective removal of H_2S by dissolving-tank vent scrubbers depends on two factors:

1. Efficiently designed and operated scrubbers
2. An alkaline scrubbing medium.

Wet-impingement venturi scrubbers are commonly used for TRS removal in dissolving-tank vent stacks. This type of scrubber is more efficient for particulate removal, but it can remove TRS as well. For alkaline scrubbing solutions at pH 13 or above, where the slope of the H_2S equilibrium line is nearly zero, the total fraction of H_2S removed in a venturi scrubber, E, can be calculated as follows *(5)*:

$$E = (y_2 - y_1)/y_2 = 1 - \exp(-N_G) \qquad (6)$$

where

E = mass-transfer efficiency for a venturi scrubber
y_2 = mole fraction of H_2S in the gas exiting the scrubber
y_1 = mole fraction of H_2S in the gas entering the scrubber

	Green liquor, g Na_2O/L	Weak wash liquor, g Na_2O/L
NaHS	31.2	6.2
NaOH	14.6	14.6
Na_2CO_3	74.2	74.2
Na_2SO_4	3.3	0.7
$Na_2S_2O_3$	3.3	0.7
NaCl	4.8	1.0

I. Typical composition of green liquor and weak wash liquor

Equation	log K
1	–1.43
2	–6.63
3	–11.78

*Source: Danko *(2)*

II. Equilibrium constants at 100°C for reactions depicted in Eqs. 1–3*

Species	Concentration
O_2, %	20.9
CO_2, %	0.4*
H_2S, ppm	5200
CO, %	0.0

*Reported as "trace"; the value 0.4% was estimated from the sensitivity of the measurement method

III. Dry gas composition measured at the shatter jets

N_G = number of overall gas-phase mass-transfer units.

The variable N_G is related to the overall volumetric gas-phase mass-transfer coefficient, $K_g a$, as

$$N_G = (K_g a R T / P_T) t_C \qquad (7)$$

where

$K_g a$ = volumetric gas-phase mass-transfer coefficient
R = ideal gas constant, 8.314 $m^3 \cdot Pa/kmole \cdot K$
T = temperature, K
P_T = total gas pressure, kPa
t_C = contact time.

N_G is typically between 1 and 2 for a venturi scrubber, so E should fall between 63% and 86% of a single equilibrium stage. Efficiencies measured on a wet-impingement venturi scrubber at one mill were 80–85% in TRS removal, with H_2S concentrations of 15–20 ppm exiting the stack.

As discussed earlier, scrubbing with green liquor should result in H_2S emissions no less than about 22±13 ppm, while scrubbing with weak wash would result in H_2S emissions no less than 12±7 ppm. The actual emissions would be higher, depending on the efficiency of the scrubber.

Lower H_2S emissions from the dissolving-tank stacks can be achieved by scrubbing with oxidized white liquor or caustic. Figure 3 shows the relationship between the H_2S concentration in the vent gases and the total concentration of sulfide in the scrubbing solution at different levels of solution pH. Scrubbing with a caustic solution of pH 11 is much more effective in removing H_2S than scrubbing with water, and it requires much less scrubbing solution per kilogram of H_2S removed.

Other TRS compounds such as methyl mercaptan, dimethyl sulfide, and dimethyl disulfide can also be present in the dissolving-tank vent gas. These organosulfur compounds are not likely to be emitted from the lower recovery furnace, but they can enter the dissolving tank from foul condensates used as makeup water.

Methyl mercaptan (CH_3SH) is weakly acidic and forms methyl mercaptide ion in alkaline solutions. Figure 4 shows the vapor pressure of methyl mercaptan in equilibrium with alkaline solutions containing 0.01N methyl mercaptan at 80°C and 100°C. As seen in Fig. 4, the equilibrium vapor pressure of methyl mercaptan decreases with increasing pH and with decreasing temperature. However, the equilibrium concentrations in the gas phase are two orders of magnitude greater than those of H_2S for the same concentrations of CH_3SH and H_2S in solution. The equilibrium vapor pressure of methyl mercaptan follows Henry's law over the range 0–0.4 mole/L methyl mercaptan, increasing linearly with the concentration of mercaptan in solution *(6)*. The relatively low amounts of methyl mercaptan in dissolving-tank vent gases can be scrubbed with alkaline solutions such as weak wash as long as the scrubbing solution is replenished continuously or frequently.

Dimethyl sulfide and dimethyl disulfide are neutral compounds and are not readily scrubbed with alkaline solutions.

Water is ineffective as a scrubbing medium for TRS removal. H_2S and methyl mercaptan are only very slightly soluble in water. Based on the data of Shih *et al. (3)*, concentration of H_2S at 1 bar total pressure over a 0.001M H_2S solution at pH 7 would be 11,000 ppm. For methyl mercaptan, the analogous concentration would be 2400 ppm. Other organosulfur TRS compounds are even less soluble in water than is methyl mercaptan, and they are not removed effectively by scrubbing with water. In practice, scrubbers operated with water will have high TRS emissions. One mill reduced its TRS emissions by 63% by switching from water to weak wash in the dis-

P_{H2O}, bar	P_{CO2}, bar	Calculated P_{H2S}, ppm
0.9	0.001	159
0.9	0.05	7950

*T = 1000K; $P_{O2} = 10^{-18}$ bar

IV. Calculated equilibrium H_2S partial pressures*

solving-tank vent scrubber.

CONCLUSIONS

The main source of TRS emissions in dissolving-tank vent gases is H_2S released by reaction of smelt and water vapor at the shatter jets. The amount of H_2S released in the shatter-jet region can be reduced by lowering the steam pressure at the shatter jets and by using more efficient shatter-jet nozzles.

The green liquor in the dissolving tank can also be a source of H_2S emissions, but the resulting H_2S concentration in the vent stack gases from green liquor will not exceed 20–25 ppm.

Organosulfur compounds (methyl mercaptan, dimethyl sulfide, etc.) may enter the dissolving tank if contaminated condensate is used in smelt dissolving or if condensates from TRS collection are disposed of in the green–white-liquor system. The relatively low amounts of methyl mercaptan in dissolving-tank vent gases can be scrubbed with alkaline solutions such as weak wash as long as the scrubbing solution is replenished continuously or frequently. However, dimethyl sulfide and dimethyl disulfide are not effectively scrubbed by alkaline solutions.

Scrubbing with an alkaline solution is the key to controlling TRS emissions from the dissolving-tank vent stacks. Caustic or oxidized white liquor are the most effective scrubbing media, followed by weak wash and green liquor. Water is not an effective scrubbing medium for green liquor. TJ

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