

## RECOVERY OF SULFIDE FROM TANNERY EFFLUENTS

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### Abstract

Investigations at pilot plant scale have shown that sulfide can be readily recovered from lime-sulfide tannery liquors in a completely enclosed system. Recovery of the sulfide is achieved by acidifying the waste to pH 4 as it is pumped into an adiabatic flash chamber under vacuum. The hydrogen sulfide gas is released into a gas absorber where it is thoroughly mixed with an alkaline solution. The experimental data show that hydrogen sulfide release follows Henry's Law. The reabsorption of the gas is accompanied by reaction with the alkali in solution. This paper presents the results of the aforementioned investigation and discusses scale-up of the process to commercial size.

### Introduction

In 1978 the Eastern Regional Research Center patented a process (1-3) for recovering sulfide which is aimed at improving safety and cost. In this process, hydrogen sulfide gas is generated in-line, quickly flashed off in a vacuum chamber, and reabsorbed in an alkali solution. This paper describes the process, reports some typical results, and discusses the theoretical aspects in sufficient detail to enable tanners to judge more readily the suitability and safety of this process and to use the information for design, scale-up, and/or operation.

#### EQUIPMENT AND PROCEDURE

Figure 1 presents a detailed flow sheet of the pilot plant process. As can be seen from this diagram, unhairing waste is first screened to remove large pieces of hide or scraps of meat and fat. When this rough-screened waste is pumped into the center of a tank, fat rises to the top by gravity. This fat is either skimmed off or pumped out at the end of the run.

From the bottom of the gravity flotation tank or grease trap, the waste is pumped at a predetermined rate while  $\text{CO}_2$  is added in-line to form  $\text{CaCO}_3$  and to adjust the pH to between 11.2 and 12.0. Thorough contact between the gas and the waste is assured through the use of an in-line mixer, and the pH is con-

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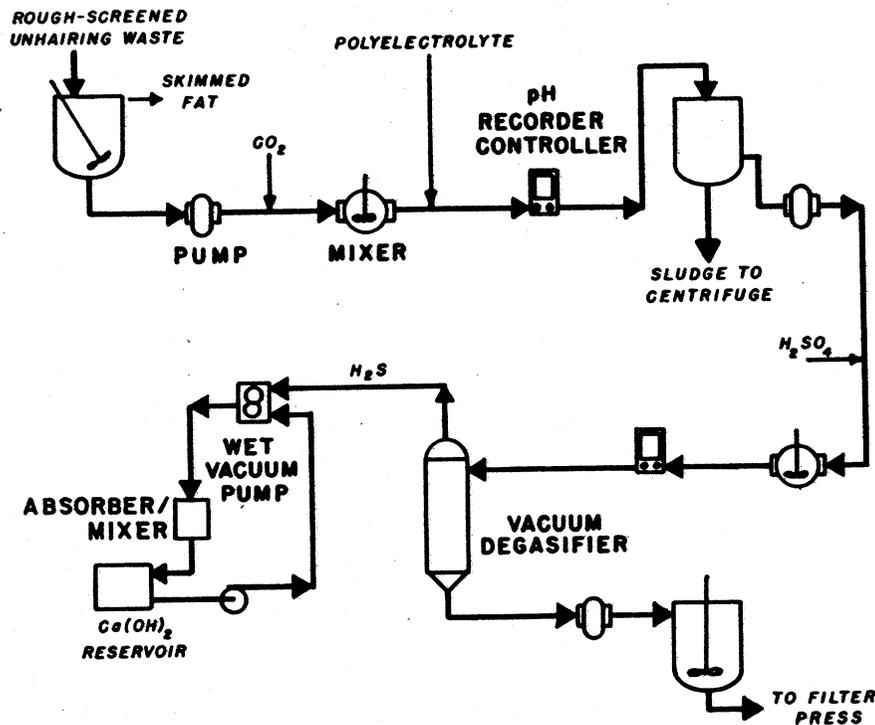


FIGURE 1. — Physico-chemical process for recovering suspended solids and sulfide from lime-sulfide unhairing wastes.

trolled with the help of a pH recorder/controller positioned further down stream. Before the  $\text{CO}_2$  sparged waste enters the next tank (or the settling tank), a suitable polyelectrolyte is added to cause flocculation of the suspended solids and settling of a thick sludge at the bottom of the tank. The supernatant from the flocculation step is slowly pumped out at a predetermined rate while sulfuric acid is metered in-line to reduce the pH to about 4. Another in-line mixer and pH recorder-controller is used to provide thorough mixing and accurate acid addition. At a pH below 4, practically all of the sulfide exists as  $\text{H}_2\text{S}$  and most of the dissolved proteins precipitate. This acidic protein slurry is then continuously degasified in a vacuum degasifier operated at about 28-29 in. Hg vacuum and provided with an agitator which helps to release the  $\text{H}_2\text{S}$  from the foam formed. The flash chamber used has a 11.5 in. diameter and a 12 in. pool depth. The slurry is introduced into the chamber through a spray nozzle to increase  $\text{H}_2\text{S}$  release. The  $\text{H}_2\text{S}$  enters two liquid ring vacuum pumps connected in series where

part of the gas is quickly reabsorbed in an alkali solution used as a sealing liquid for the pumps. The alkaline solution is stored in a 100-gal reservoir and recycled through the vacuum pumps and an absorber mixer where the rest of the gas is absorbed. The degasified slurry is pumped from the bottom of the vacuum degasifier into a closed tank vented into the bottom of the 100-gal tank. A chemical oxidizing agent such as sodium peroxide is added to the tank with mixing to destroy the small amounts of  $H_2S$  which remain in the liquid after degasification (4). Finally, the protein slurry is dewatered in a solid bowl centrifuge or a filter press.

To study the effect of operating conditions on the degree of  $H_2S$  absorption, the waste flow rates were varied from 15 to 30 gal per hour, the temperature of the unhairing waste was varied from 60°F to 150°F, the absolute pressure in the vacuum chamber from 0.9 to 5 in. Hg and the pH from 2 to 4. The  $Na_2S$  concentration of the wastes ranged between 0.4 and 1.0 percent.

To study the rate of absorption of the  $H_2S$  in alkali, lime slurries and solutions containing 1 percent NaOH were utilized. The volume of the alkaline solutions employed was 60-80 gal. The lime slurries were recirculated through the gas absorption system (the vacuum pumps and the mixer) at 3-3.5 gal/min while the sodium hydroxide solution recirculation rate was about 0.8-1.0 gal/min.

Samples of the waste being treated were taken for sulfide analysis before clarification, and after clarification and degasification (before the waste returned to the storage tank). In addition, the rate of  $H_2S$  recovery was monitored by pH recordings and by occasional analysis of the sulfide content in the reservoir.

## Results

Table I presents the results obtained during a typical pilot plant experiment. The composition of the original waste is in line 1. The 2nd line shows the composition after screening; this removes a substantial quantity of fat, especially if the waste was obtained by processing fresh hides. Line 3 shows that the waste volume increased somewhat due to the addition of the polyelectrolyte solution. This resulted in a small decrease in composition of the soluble components (such as  $Na_2S$ ) in the supernatant (line 4). The sludge (line 5) contains most of the lime originally presented in the waste as well as fat and protein.

Line 6 of Table I shows that injection of a properly acidified and mixed supernatant into the vacuum degasifier at 1.1 in. Hg absolute pressure flashed off the  $H_2S$  reducing the  $Na_2S$  content by 97% to 139 ppm. This  $H_2S$  was quickly reabsorbed in the lime slurry (line 7) which circulated through the liquid ring pump as a sealing liquid. A material balance for  $H_2S$  showed that practically all of the released portion was captured by the lime slurry.

As can be seen from Table II,  $H_2S$  desorption was found to be only slightly dependent on the pH provided it was below 4.0. At 1.62 in. Hg absolute pressure, the percent  $Na_2S$  remaining in the degasified supernatant decreased from 205 ppm to 166 ppm when the pH was decreased from 4.0 to 2.0.

**TABLE I**  
**DEGASIFICATION OF UNHAIRING WASTE**  
**(FROM FRESH HIDES PROCESSED IN PADDLES)**

Treatment step	Volume (1)	Total solids (%)	Ca** (% w/w)	TKN (% w/w)	Na <sub>2</sub> S (ppm, w/v)	Fat (% w/w)
<b>A. UNHAIRING WASTE</b>						
Original waste	120	4.36	0.372	0.251	5075	0.85
After screening and skimming of fat	117	3.66	0.326	0.224	5101	0.495
After CO <sub>2</sub> + Jaguar C-13*** addition	125					
After settling:						
Supernatant	96.8	2.47	0.042	0.220	4603	0.265
Sludge	28.6	5.87	0.86	2.37	5062	1.52
After acidifying and degasify- ing** of supernatant	97.2				139	
<b>B. ABSORBING SOLUTION</b>						
Original	251	0.903	0.488		0	
After desorption of H <sub>2</sub> S from waste	251	1.094	0.488		1906*	

\* After desorption pH dropped from 12.6 to 12.35.

\*\* At 6% and 1.1 in. Hg absolute pressure.

\*\*\* Polyelectrolyte made by Stein-Hall.

**TABLE II**  
**EFFECT OF pH ON DEGASIFICATION OF PROTEIN SLURRIES\***

pH	Na <sub>2</sub> S remaining, ppm
2	166
3	157
4	205

\* Vacuum = 28.3 in. Hg.

Temperature = 76°F.

Variation in temperature was observed to have a somewhat greater effect on the degree of H<sub>2</sub>S desorption. When the temperature of the supernatant was increased from 60° to 150°F before the supernatant was subjected to a pressure of 1.32 in. Hg, the amount of sodium sulfide which remained in the liquid phase after degasification decreased from 255 to 95.7 ppm (Table III).

**TABLE III**  
**EFFECT OF TEMPERATURE OF DEGASIFICATION OF PROTEIN SLURRIES\***

Temp. °F	Na <sub>2</sub> S remaining, ppm
60	285
74	138
100	140
140	68.3
140 (repeat)	95.3

\* Vacuum in flashing chamber = 28.6 in. Hg. pH = 4.2.

The most important variable, as can be seen from Table IV, was the operating pressure. A reduction from 1122 to 148 ppm in the Na<sub>2</sub>S concentration was ac-

TABLE IV

EFFECT OF OPERATING PRESSURE ON DEGASIFICATION OF PROTEIN SLURRIES\*

Degasifier vacuum, in. Hg	Na <sub>2</sub> S Remaining ppm
29	148
27.2	415
25.1	1122

\* pH = 4.0.  
Temp. 75°-76°F.

complished by decreasing the operating pressure in the vacuum chamber from 4.82 to 0.92 in. Hg while maintaining the pH at 4.0 and the temperature between 75° and 76°F.

### Discussion

#### A. PRESSURE BUILDUP DURING ACIDIFICATION OF WASTE

Raoult's Law applies to water vapor at equilibrium with a body of water as follows:

$$P_{H_2O} = \Pi_{H_2O} X_{H_2O}, \quad (1)$$

where

$P_{H_2O}$  = partial pressure of water in vapor

$\Pi_{H_2O}$  = vapor pressure of water

$X_{H_2O}$  = mole fraction of water in the liquid

and Henry's Law applies to the gases dissolved in unhairing wastes after acidification:

$$P_{H_2S} = H_{H_2S} X_{H_2S} \quad (2)$$

and

$$P_{air} = H_{air} X_{air},$$

where H is the Henry's Law constant which is equal to 496 atm per mole fraction

for  $H_2S$  and to 67,500 atm per mole fraction for air at  $21^\circ C$ . If a 0.5 percent solution of  $Na_2S$  at  $21^\circ C$  is acidified in a tight container, the following pressure results:

$$P_{H_2S} = H_{H_2S} X_{H_2S} = 496 (0.00116) = 0.574 \text{ atm}$$

$$P_{air} = 67,500 (1.47 \cdot 10^{-5}) = 0.992 \text{ atm}$$

$$P_{H_2O} = \Pi_{H_2O} X_{H_2O} = \frac{18.7 \text{ mm}}{760 \text{ mm/atm}} (0.999) = 0.0246 \text{ atm,}$$

or a total of only

$$P_t = P_{H_2S} + P_{air} + P_{H_2O} = 1.59 \text{ atm,}$$

a pressure which can be handled safely in most types of equipment and piping.

#### B. DESORPTION OF $H_2S$ from Waste by Adiabatic Flashing

As the acidified waste enters the vacuum chamber, the  $H_2S$  is stripped from it because under vacuum the partial pressure of the gas at the surface is lower than in the bulk of the liquid. Indeed, the degree of supersaturation is so large that gas bubbles form in the interior of the liquid and much of the gas escapes by diffusing to the surface of the bubbles. This bubble formation complicates the operation considerably because the waste contains proteins and other surface active agents which render the bubbles fairly stable. Cured hide wastes yield more foam than fresh wastes probably because the latter contain more fat which acts as an anti-foaming agent. Of course, addition of antifoams was found to decrease the stability of the bubbles of both types of wastes. Theoretically,  $H_2S$  desorption is similar to flash distillation encountered in petroleum engineering. Just as in the sizing of drums for flash distillation, one of the following operations can be rate controlling: de-entrainment of liquid from vapor, elimination of vapor from liquid, and the requirements of downstream equipment. In the case of  $H_2S$  desorption from unhairing waste, elimination of gas and vapor from the flash liquid is the controlling factor because of the stability of the bubbles formed. Whereas the residence time usually recommended for flash distillation of foaming liquids is about 5 min, the residence time used in the pilot plant was 17 min during  $H_2S$  desorption from fresh hide waste without addition of an antifoaming agent.

A material balance for flash desorption gives

$$F = V + L, \quad (3)$$

where F, V, L = total quantity of  $H_2S$  gas, water, and air in the feed, the vapor phase, and degasified liquid, respectively.

For any component, j,

$$FZ_j = VY_j + LX_j \quad (4)$$

where  $Z_j$ ,  $Y_j$ , and  $X_j$  = concentration of component j in the feed, vapor, and degassed liquid, respectively. Assuming, as before, that Raoult's Law applies to water vapor at equilibrium with a body of water and that Henry's Law, eq. (2), applies to the gases (i.e.,  $H_2S$  and air) dissolved in the water, it can be seen that, in general,

$$Y_j = \frac{p_j}{P_t} = \frac{H_j}{P_t} X_j \quad (5)$$

or

$$Y_j = K_j X_j \quad (6)$$

where j is any component of the gas and water mixture and  $K_j$  = constant at a given total pressure and temperature. Eliminating F from eqs. (3) and (4) yields

$$\frac{L}{V} = \frac{Y_j - Z_j}{Z_j - X_j} \quad (7)$$

Then, solving for  $Y_j$ , and using eq. (6)

$$Y_j = \frac{Z_j \frac{L}{V} + 1}{1 + \frac{L}{VK_j}} \quad (8)$$

and observing that for equilibrium vaporization (Treybal (5))

$$\sum Y_j = 1, \quad (9)$$

eq. (8) can be solved by assuming values for  $\frac{L}{V}$  and solving for  $Y_j$  of each component in the vapor phase until eq. (9) is satisfied.

Such a calculation is shown in Table V for degassing 19 gal per hour of unhairing waste containing 0.5 percent  $Na_2S$  by adiabatic flashing at 21°C and 1.5 in. Hg absolute pressure. In terms of mole fraction, the waste contains:

$$Z_{H_2O} = 0.9988 \frac{\text{moles } H_2O}{\text{mole of solution}} ; Z_{H_2S} = 0.001158 \frac{\text{moles } H_2O}{\text{mole solution}}$$

TABLE V

## DESORPTION OF HYDROGEN SULFIDE FROM UNHAIRING WASTE

Waste component	$K_j$	$\frac{\text{mole fraction in gas}}{\text{mole fraction in liquid}}$	$Z_j$	$Y_j$	$\frac{L}{V} = 455$
Water		$\frac{P_{H_2O}}{P_t} = \frac{18.7}{38.10} = 0.491$	0.9988	0.491	
H <sub>2</sub> S		$\frac{H_{H_2S}}{P_t} (760) = \frac{(496) 760}{38.10} = 9893$	0.001158	0.505	
Air		$\frac{H_{Air}}{P_t} (760) = \frac{67500 (760)}{38.10} = 1.35 * 10^{-6}$	$1.47 * 10^{-5}$		
				$\frac{0.007}{\Sigma Y_j} = 1.003$	

Operating conditions: Temperature = 21°C

Absolute pressure during desorption = 1.5 in. Hg  
= 38.10 mm Hg

Waste flow rate: 19 gal/hr  
Na<sub>2</sub>S concentration = 0.5%

and

$$Z_{air} = 1.47 * 10^{-5} \frac{\text{moles air}}{\text{mole solution}}$$

(The solubility of the air in the solution was obtained from Lange's Handbook of Chemistry, 12th ed., p. 10-3.) Table V shows that the vapor which escapes contains 0.491 moles of H<sub>2</sub>O, 0.505 moles of H<sub>2</sub>S, and only 0.007 moles of air per mole of vapor. The ratio of  $\frac{L}{V} = 455$  means that only  $\frac{1}{456} (100) = 0.22$  percent of the feed is vaporized (mostly as H<sub>2</sub>S). Most interestingly, however, the H<sub>2</sub>S concentration of the desorbed liquid is

$$\begin{aligned} X_j &= \frac{Y_j}{K_j} = \frac{0.505 \text{ moles H}_2\text{S/mole vapor}}{9893 \text{ mole fraction vapor/mole fraction liquid}} \\ &= 5.10 * 10^{-5} \text{ moles H}_2\text{S/mole liquid} \\ &= 96.5 \text{ ppm H}_2\text{S} \\ &= 221 \text{ ppm Na}_2\text{S.} \end{aligned}$$

This value is in general agreement with values obtained experimentally at other pressures and temperatures (Tables II to IV).

### C. RECOMPRESSION OF EVOLVED GAS

From the vacuum chamber, the gas mixture enters a liquid ring vacuum pump. While leaving this pump the mixture is recompressed to slightly above atmospheric pressure. If produced from waste containing 0.5 percent  $\text{Na}_2\text{S}$ , 1 g mole of the mixture contains 0.491 g mole of water, 0.505 g mole of  $\text{H}_2\text{S}$ , and 0.007 g mole air (see Table V). As soon as the pressure is raised, the water vapor in the bubbles condenses and mixes with the liquid solution leaving the pump, and the  $\text{H}_2\text{S}$ , which starts to diffuse into the solution, reacts instantaneously with the alkali.

The composition of the condensate is given as follows:

$$X_j = \frac{Z_j \frac{L}{V} + 1}{K_j + \frac{L}{V}} \quad (10)$$

At the point of condensation,  $\sum X_j = 1.0$  (Treybal (5)). The calculations are summarized in Table VI. Note that the gas mixture generated under vacuum is

TABLE VI

RECONDENSATION OF FLASHED VAPOR				
Component	$K_j$	$Z_j$	$X_j$	$Y_j$
Water	$\frac{18.7}{760} = 0.0246$	0.491	$\frac{0.491(0.95 + 1)}{0.0246 + 0.95} = 0.9980$	0.02455
$\text{H}_2\text{S}$	496	0.505	0.0019	0.9424
Air	67,500	0.007	$\frac{2 \cdot 10^{-7}}{\sum X_j = 1.0000}$	$\frac{0.0135}{\sum Y_j = 0.980}$

now condensed, therefore, the  $Y_j$  gas compositions of Table V appear as  $Z_j$  (feed) concentration of Table VI. It is significant that the condensate contains practically pure water ( $X_j = X_{\text{water}} = .998$  mole fraction) while the remaining uncondensed gas contains almost pure  $\text{H}_2\text{S}$  ( $Y_j = Y_{\text{hyd. sulfide}} = 0.9424$  mole fraction). In other words, Table VI shows that the recompressed mixture, which is at a pressure slightly above atmospheric, contains bubbles of almost 100 per cent  $\text{H}_2\text{S}$  gas.

#### D. REABSORPTION OF HYDROGEN SULFIDE IN ALKALI

Addition of alkali to water not only increases its capacity to absorb  $\text{H}_2\text{S}$ , but increases the rate of absorption as well. Different results are obtained depending on the alkali concentration, the type of alkali, and the mode of operation. It is, of course, of utmost importance that the absorption process be well understood and conducted under conditions that ensure practically no release of  $\text{H}_2\text{S}$  to the atmosphere.

#### THEORY OF GAS-LIQUID REACTION

When  $\text{H}_2\text{S}$  gas reacts with  $\text{OH}^-$  ion, the following reactions occur:



and



The concentrations of the sulfide species are governed by the following relationships:

$$\frac{[\text{HS}^-]}{[\text{OH}^-][\text{H}_2\text{S}]} = 10^7 \quad (13)$$

$$\frac{[\text{S}^{2-}]}{[\text{HS}^-][\text{OH}^-]} = 1, \quad (14)$$

as well as by the mass balance in sulfide species

$$S_T = \text{HS}^- + \text{S}^{2-} + \text{H}_2\text{S}, \quad (15)$$

and by the condition of electroneutrality

$$nM_o = \text{OH}^- + \text{HS}^- + 2\text{S}^{2-}, \quad (16)$$

where  $M_o$  = concentration of the positive ion of the alkali used and  $n$  is its valency.

When hydrogen sulfide reacts with an alkali, the pH decreases to moderate levels at which the  $[\text{S}^{2-}]$  is very low. Consequently, eqs. (12) and (14), and the  $[\text{S}^{2-}]$  in eqs. (15) and (16) can be ignored. Solution of eqs. (16) and (13) then yields

$$[\text{HS}^-] = \frac{10^7 [\text{H}_2\text{S}] nM_o}{1 + 10^7 [\text{H}_2\text{S}]} \quad (17)$$

In absorption, it is necessary to distinguish between batch and steady flow pro-

cesses. For fast reversible reactions in absorbers (6),

$$\tau = \int_{B^{\circ}(o)}^{B^{\circ}(t)} \frac{dB^{\circ}}{\bar{R}a'z}, \quad (18)$$

where

$B^{\circ}(o)$  is the initial value, and  $B^{\circ}(t)$  the value at time  $t$  of a substance  $B$  which reacts with the dissolved gas.

$\bar{R}$  = average rate of gas absorption into agitated liquid, per unit area of surface.

$a'$  = area of interface between the gas and the liquid per unit volume of the system, here assumed to be  $2.5 \text{ cm}^2/\text{cm}^3$  (7).

$\tau$  = residence time in the absorber (in sec).

$z$  = the stoichiometric coefficient of the reagent (in this discussion the number of  $\text{OH}^-$  ions which reacts with  $\text{H}_2\text{S}$ ).

In a situation in which  $\bar{R}a'$  remains constant, eq. (11) can be integrated to yield

$$\tau = \frac{B^{\circ}(o) - B^{\circ}(t)}{\bar{R}a'z} = \frac{B_i - B^{\circ}}{\bar{R}a'z}, \quad (19)$$

where  $B_i$  and  $B^{\circ}$  are the inlet and outlet concentrations of the reagent which reacts with the gas.

The volume,  $W$ , of the absorber can be obtained from the expression

$$W = \frac{q}{\bar{R}a'z}, \quad (20)$$

where  $q$  = the rate of introduction of gas into the absorber.

The flow rate,  $v$ , of the reagent into the absorber is equal to

$$v = \frac{W}{\tau} \quad (21)$$

Equations (19) to (21) can be solved for  $q$  yielding

$$q = 10^{-3} (B_i - B^{\circ}) v. \quad (22)$$

When an absorbed gas undergoes an instantaneous reaction, as does  $\text{H}_2\text{S}$  with an alkali in solution, and the diffusivities of the reactant and product are equal,

the rate of absorption is equal to (9)

$$\bar{R}a'z = k_L a' \Delta C, \quad (23)$$

where

$k_L$  = liquid film mass-transfer coefficient for physical absorption = 0.04 cm/sec (8).  $\Delta C$  = the amount of gas required to physically and chemically saturate a unit volume of the bulk liquid to a partial pressure equal to that at the interface.

Letting  $[H_2S]^\circ$  = unreacted  $H_2S$  present in the absorbing solution at a given point in time,  $[HS^-]^\circ$  = reacted  $H_2S$  present at that time in the absorbing solution, while  $[H_2S]^*$  and  $[HS^-]^*$  = unreacted and reacted  $H_2S$ , respectively, which will be present after saturation is achieved,  $\Delta C$  becomes

$$\Delta C = [H_2S]^* + [HS^-]^* - [H_2S]^\circ - [HS^-]^\circ. \quad (24)$$

To solve eqs. (23) and (24), it is necessary to know  $[H_2S]^*$ ,  $[HS^-]^*$ ,  $[H_2S]^\circ$ ,  $[HS^-]^\circ$ , as well as  $k_L$  and  $a'$ . Under the constraints assumed in this paper,  $[H_2S]^*$  is a function of the pressure attained during recompression and has a constant known value for the equipment selected.

It was shown previously that when the evolved gas is recompressed, the uncondensed fraction contains almost pure  $H_2S$  at atmospheric pressure. The condensed liquid is saturated with  $H_2S$  as is the interface between the gas bubbles and the rest of the solution. This  $H_2S$  concentration at saturation can be calculated with Henry's Law, eq. (2), which yields

$$X_{H_2S} = \frac{P_{H_2S}}{H_{H_2S}} = \frac{1 \text{ atm}}{496 \frac{\text{atm}}{\text{mole fraction}}},$$

therefore

$$[H_2S]^* = 0.11 \frac{\text{moles}}{\text{liter}}.$$

As will be shown below,  $[H_2S]^\circ$  varies little in a once through operation, but varies with time if the alkaline reabsorption liquid is recirculated.

#### ABSORPTION OF HYDROGEN SULFIDE GAS INTO RECYCLED SOLUTIONS OF ALKALI

Initially the recycled alkaline solution in the storage tank contains no hydrogen

sulfide and gas absorption is relatively fast. As the  $[\text{HS}^-]$  ion in the solution rises, the rate of  $\text{H}_2\text{S}$  gas absorption decreases. According to eq. (22), therefore, the rate of recycling,  $v$ , should be continuously increased with time to assure adequate gas removal in the absorber. To avoid this processing complication, the rate of recycling was kept high enough to ensure adequate gas absorption until the solution was replaced.

Two operating rules were followed to ensure safety. According to the first rule, the concentration of  $\text{H}_2\text{S}$  in the air above the open storage tank containing the alkali used in the  $\text{H}_2\text{S}$  absorption unit was not permitted to exceed 2.0 ppm. The solution was replaced before this  $\text{H}_2\text{S}$  concentration in the air was reached. According to the second safety rule, the  $\text{H}_2\text{S}$  in the solution entering the open storage tank from the absorber/mixer unit was kept below  $1.1 \times 10^{-6}$  g moles/liter to prevent escape of  $\text{H}_2\text{S}$  into the air at concentrations higher than 10 ppm which is regarded to be hazardous for 8 hr of exposure.

For operating conditions satisfying safety rule #1,  $[\text{H}_2\text{S}] = [\text{H}_2\text{S}]_1 = 2.24 \times 10^{-7}$  (calculated using Henry's Law), and eq. (17) yields:

$$[\text{HS}^-]_1 = 0.691 \text{ nMo.} \quad (25)$$

For operating conditions satisfying safety rule #2, where  $[\text{H}_2\text{S}]_2 = 1.1 \times 10^{-6}$ , eq. (17) yields:

$$[\text{HS}^-]_2 = 0.917 \text{ nMo.} \quad (26)$$

Therefore, the permissible increase in  $[\text{HS}^-]$  in the solution,  $x$ , can be readily calculated as:

$$x = [\text{HS}^-]_2 - [\text{HS}^-]_1 = (0.917 - 0.691) \text{ nMo.} \quad (27)$$

Examination of eq. (27) reveals that  $x$  increases with increase in concentration of the alkali. It is also a function of the difference in  $[\text{H}_2\text{S}]$  achieved in one passage of the solution through the absorber. Since  $x \approx B_i - B^o$ , eq. (22) can be used to calculate the minimum recycling rate satisfying both safety conditions simultaneously:

$$v_m = \frac{q}{10^{-3} x} \quad (28)$$

To follow the changes which occur during recycling of a solution of an alkali of limited solubility, it is necessary to use the solubility product. For lime, for example,

$$[\text{Ca}^{++}][\text{OH}^-]^2 = 3.7 \times 10^{-5} \text{ at } 25^\circ\text{C} \quad (29)$$

which shows that a freshly prepared saturated lime solution contains

$$[\text{Ca}^{++}] = .021 \text{ g moles/liter and } [\text{OH}^-] = 0.42 \text{ g moles/liter (pH} = 12.6).$$

The solubility product is most probably not satisfied in a slurry leaving the absorber/mixer. As hydrogen sulfide is added, more of the lime will dissolve in the second reaction stage (taking place in the storage tank) and will raise the  $[\text{OH}^-]$  towards a new equilibrium.

Using eqs. (13), (16), and (29), it can be shown that the first safety condition is reached when  $[\text{Ca}^{++}]_1 = 0.0460$ ,  $[\text{OH}^-]_1 = 0.0284$  (pH = 12.45),  $[\text{HS}^-]_1 = 0.0636$ , and  $\Delta C = 0.11 + (0.0284 + 0.0636) - 0.0636 = 0.138$ .

To ensure simultaneous compliance with the second safety rule, no dissolution of lime in the passage of the slurry through the absorber is assumed; consequently, in the calculation of  $[\text{HS}^-]_2$  the same value for  $[\text{Ca}^{++}]$  is used as in the calculation of  $[\text{HS}^-]_1$ :

$$[\text{HS}^-]_2 = 0.917 (2) (0.046) = 0.08436$$

and therefore:

$$x = 0.08436 - 0.0636 = 0.0208.$$

Also, from eq. (13):

$$[\text{OH}^-]_2 = \frac{[\text{HS}^-]}{10^7 (\text{H}_2\text{S})} = \frac{0.08436}{10^7 (1.1 * 10^{-6})} = 0.00767,$$

and using eq. (24):

$$\Delta C = 0.11 + (0.00767 + 0.08436) - 0.08436 = 0.118.$$

Using the calculated values for  $\Delta C$  and  $x$ , eqs. (19) to (22) and eq. (28) can be used to solve for  $W$ ,  $\tau$ , and  $v_m$  for known values of  $q$ , and vice versa.

#### EXPERIMENTS WITH LIME SLURRIES

Sodium hydroxide is almost as expensive as sodium sulfide. It is economical to utilize the cheaper lime for recovering hydrogen sulfide. However, lime solutions are low in  $\text{OH}^-$  ion content while absorption of  $\text{H}_2\text{S}$  by lime slurries involves three phases (gas, liquid, and solid) and is, therefore, somewhat complex. After diffusing into the liquid phase,  $\text{H}_2\text{S}$  reacts with lime slurries in two stages. In the first stage it reacts almost instantaneously with the  $\text{OH}^-$  present in solution. Most of the hydroxyl ions which have reacted are then replaced in the second, slower reaction stage, which involves dissolving of solid lime, diffusion of the ions into the bulk of the liquid, as well as some additional reaction of  $\text{H}_2\text{S}$  with  $\text{OH}^-$  to bring about a new equilibrium between the phases.

Recycling was studied in this work with the hope of taking advantage of the dual reaction mechanism which occurs when  $\text{H}_2\text{S}$  is absorbed by lime solutions. The recycling process was designed to include an absorber/reactor with maximum agitation to carry out the first stage absorption and instantaneous reaction, and a storage tank provided with a minimum amount of mixing to store the slurry and to keep the lime particles suspended while carrying out the second stage reaction.

Equations (20) to (22) give the absorption rate only for the first reaction stage in the absorber/mixer, because dissolution of lime, which takes place in the second stage, can be so slow under most conditions as to be rate controlling.

Since the  $\Delta C$  values for the two safety conditions decreased only moderately (from 0.138 to 0.118, as calculated above), eqs. (19) to (22) were assumed to be applicable for calculating changes induced by the passage of the lime slurry once through the absorber; and eq. (28) was used to calculate the minimum recirculation rate using the above calculated value for  $x$ .

During the experiments, the lime slurry recycling rate was kept constant at 200  $\text{cm}^3/\text{sec}$ . The  $\text{H}_2\text{S}$  gas release from the unhairing waste was slowly increased from  $q = 0.971 \times 10^{-3} \text{ cm}^3/\text{sec}$  to  $q = 3.88 \times 10^{-3} \text{ cm}^3/\text{sec}$ . The theoretical minimum recycling rates,  $v_m$ , calculated from eq. (28) for the lime slurry were thus varied from 47 to 187  $\text{cm}^3/\text{sec}$  and made to approach the experimental recycling rate of 200  $\text{cm}^3/\text{sec}$ . The lime slurry was recycled and reused until the  $\text{H}_2\text{S}$  odor in the pilot plant became perceptible, and darkening of wetted lead acetate paper was visible above the solution in the reservoir. This occurred when the sulfide concentration in the storage reservoir had increased to about 0.2 percent and about 2.6 ppm  $\text{H}_2\text{S}$  was present in the atmosphere above the slurry. The fact that no  $\text{H}_2\text{S}$  odor was released prematurely into the atmosphere during these experiments confirms the soundness of the theoretical approach used in the design of the process.

Commercial unhairing wastes usually contain about 0.2 percent sulfide (0.5 percent  $\text{Na}_2\text{S}$ ). At a flow rate of 19 gal per hr (a flow rate found suitable for fresh hide waste without addition of antifoaming agent), the gas was generated in the flash chamber at a rate,  $q = 1.23 \times 10^{-3} \text{ g moles H}_2\text{S per sec}$ . With  $x = 0.0208$  (as shown above), the minimum theoretical recycling rate was:

$$v_m = \frac{q}{10^{-3} x} = \frac{1.23 \times 10^{-3}}{10^{-3} (0.0208)} = 59 \frac{\text{cm}^3}{\text{sec}}$$

and since

$$\begin{aligned} \bar{R}a'z &= k_L a' \Delta C = 0.04 (2.5) \frac{0.118 + 0.138}{2} 10^{-3} \\ &= 1.28 \times 10^{-5} \text{ g moles per cm}^3 \text{ per sec.} \end{aligned}$$

$$\tau = \frac{B_i - B^o}{\bar{R}a'z} = \frac{0.0208 * 10^{-3}}{1.28 * 10^{-5}} = 1.6 \text{ sec}$$

and

$$W = \frac{q}{\bar{R}a'z} = \frac{1.23 * 10^{-3}}{1.28 * 10^{-5}} = 96 \text{ cm}^3.$$

It can be readily calculated from the above data that for a tannery processing 1000 hides per day and generating 25,000 liter of unhairing waste containing 0.5 percent  $\text{Na}_2\text{S}$ , which is being degassed in 8 hr, the slurry recycle rate,  $v$ , would have to be 9242 liter/hr and the volume of the absorber/mixer,  $W$ , equal to 4.2 liters.

#### EXPERIMENTS WITH SODIUM HYDROXIDE SOLUTIONS

When the process of unhairing waste containing 0.5 percent sodium sulfide was acidified and degasified under vacuum, the hydrogen sulfide gas was generated in the flash chamber at rates ranging between  $0.972 \times 10^{-3}$  and  $3.38 \times 10^{-3}$   $\text{cm}^3/\text{sec}$  as during the tests with the lime slurries. The evolved gas was absorbed in about 250 liter of a 1 percent solution of sodium hydroxide which was recycled at a constant rate of 50  $\text{cm}^3/\text{sec}$  through the vacuum pump to the absorber/mixer, and then into the storage reservoir. A steady decrease in the pH of the solution was observed with time. At approximately pH 12.9, a hydrogen sulfide odor became perceptible near the open storage tank and wetted lead acetate paper held above the solution in the storage tank showed some discoloration. When analyzed, a sample of the solution in the reservoir was found to contain about 0.5 percent sulfide. Using eq. (13) and the neutrality condition  $[\text{Na}^+] = [\text{OH}^-] + [\text{HS}^-]$ , it was calculated that the contents of the storage tank were close to reaching the first safety condition corresponding to  $[\text{OH}^-]_1 = 0.0794$ ,  $[\text{HS}^-]_1 = .171$ , and  $[\text{H}_2\text{S}]_1 = 2.2 \times 10^{-7}$  g moles/liter, and 0.53 percent sulfide. The fact that the odor was not perceived earlier demonstrates that the gas was well absorbed and dissolved in the vacuum pump and the absorber/mixer before it entered the storage tank. (Some escape of  $\text{H}_2\text{S}$  occurred only when the absorber/mixer was bypassed.) The reaction was safe; after the odor was detected it could be easily stopped before proceeding further. An additional pass through the absorber would have increased the  $[\text{H}_2\text{S}]$  concentration of the air above the reservoir only to 3.2 ppm. This is true because of the high ratio of sodium hydroxide solution recirculated to unhairing waste degasified.

When the experiment was discontinued,  $x$  was only equal to 0.0244:

$$x = \frac{q}{v(10^{-3})} = \frac{1.23 \times 10^{-3}}{(50)(10^{-3})} = 0.0244 \text{ g moles/liter.}$$

However, if the run had been carried out under conditions previously defined as safe (i.e., at minimum recycling rate),  $x$  would have been much higher:

$$x = [\text{HS}^-]_2 - [\text{HS}^-]_1 = (0.917 - 0.691)(1)(0.25) = 0.0565$$

and

$$v = \frac{1.23 \times 10^{-3}}{0.0565 \times 10^{-3}} = 21.8 \text{ cm}^3/\text{sec} = 75.61 \text{ liter/hr.}$$

Under these conditions:

$$\begin{aligned}\Delta C &= [0.11 + 0.0794 + 0.171 - 0.171] \\ &= 0.189\end{aligned}$$

$$\bar{R}a' = (0.040) (2.5) (1.89 * 10^{-4}) = 1.89 * 10^{-5}$$

$$W = \frac{q}{Ra'z} = \frac{1.23 * 10^{-3}}{1.89 * 10^{-5}} = 66 \text{ cm}^3,$$

$$\tau = \frac{.0585 * 10^{-5}}{1.89 * 10^{-5}} = 3.09 \text{ sec.}$$

Therefore, a tannery generating 25,000 liter of waste and degassing it in 8 hr, would need to recycle a 1 percent NaOH solution at the rate of

$$\begin{aligned}v, \text{ tannery} &= 75.6 \text{ liter/hr} \frac{25,000 \text{ liter}}{(8 \text{ hr}) (19 * 3.78) \text{ liter/hr}} \\ &= 3289 \text{ liter/hr} \\ &= 14 \text{ gal/min}\end{aligned}$$

which is a nominal amount. The use of sodium hydroxide solution at concentrations higher than 1 percent would even further decrease the recycling rate.

### Summary and Conclusions

The results of the study show that the sulfide recovery process described follows the gas laws and kinetic theory closely and is safe and effective for removing and recovering practically all of the  $H_2S$  in tannery unhairing wastes if the process is well constructed and operated. The calculations presented show that very little pressure is produced during the  $H_2S$  release. It is recommended, therefore, that the pipes, pumps, and tanks be made of plastic to prevent corrosion.

The vacuum chamber and the associated pipes should be checked regularly to assure that there are no major air leaks in the system. The presence of excessive amounts of air would cause the capacity of the vacuum pump to be exceeded and would increase the gas phase interfacial resistance (which in the absence of air is negligible) causing insufficient absorption of gas in the absorber/reactor. In the design of the absorber/reactor, precautions should be made to prevent such occurrences.

The liquid-ring type pump has not justified itself completely as both a source of very high vacuum and an efficient absorber/reactor. It may be desirable, there-

fore, to replace it with a reciprocating (piston) vacuum pump which would ensure a vacuum high enough to minimize the peroxide treatment for oxidizing the traces of  $H_2S$  remaining in the waste after degasification. A separate gas absorber should be provided with sufficient agitation to ensure thorough mixing of two phases and efficient absorption of the gas.

While some tanners may prefer using a lime slurry for absorbing the released  $H_2S$ , a concentrated solution of NaOH appears to be attractive because of the simplicity and compactness of the operation. As explained above, absorption into a lime slurry involves three phases and necessitates recycling of the slurry at a constant rate, whereas absorption into a concentrated sodium hydroxide solution involves only two phases (gas and liquid) and the capacity to react instantaneously with the absorbed  $H_2S$  is quite high. A holding tank for about 10,000 liters of 1.0 percent NaOH solution, a vacuum chamber with a 17-min residence time, a vacuum pump with a capacity of at least 750 liters of gas per minute at 50 mm Hg absolute pressure, and an absorber/mixer of about 3-liter capacity are the main pieces of equipment needed for an operation processing unhairing waste from a 1000 hide/day tannery.

### Nomenclature

$a'$  = interfacial area per unit volume of liquid, here assumed equal to  $2.5 \text{ cm}^2/\text{cm}^3$ .

$B_i, B^o$  = inlet and outlet concentrations of  $[OH^-]$  in the alkaline solution passing once through the absorber/reactor.

$B^o(O), B^o(t)$  = initial  $OH^-$  concentration and its concentration at time  $t$  in the alkaline solution passing once through the absorber/reactor.

$\Delta C$  = the amount of gas required to physically and chemically saturate a unit volume of the alkaline solution to a partial pressure equal to that at the interface.

$F$  = quantity of feed, moles per hour per unit chamber cross-section.

$H$  = Henry's Law constant, for hydrogen sulfide equal to 496 atm/mole fraction at  $21^\circ\text{C}$ , for air equal to 67,500 atm/mole fraction.

$K_j$  = mole fraction in gas/mole fraction in liquid.

$k_L$  = liquid-side mass-transfer coefficient assumed to be equal to  $0.04 \text{ cm/sec}$ .

$L$  = quantity of degasified liquid, moles per hour per unit chamber cross-section.

$M_o$  = concentration of positive ion of alkali.

$n$  = valence of positive ion of alkali.

$\Pi$  = vapor pressure of pure component  $j$ , atm.

$P_r$  = total pressure, atm.

$p_j$  = partial pressure of component  $j$  in vapor, atm.

$q$  = rate of release of  $H_2S$  in vacuum chamber.

$\bar{R}_a'$  = rate of absorption per unit volume of liquid.

$S_T$  = sum of the concentrations of all molecular and ionic species containing sulfide.

$V$  = quantity of vapor, mole per hour per unit of chamber cross-section.

$v$  = flow rate or recirculation of alkaline solution through the absorber/reactor.

$v_\phi$  = flow rate of the acidified waste.

$W$  = liquid capacity of absorber/reactor.

$W_\phi$  = liquid volume in degasifier.

$X_j, Y_j, Z_j$  = concentration of component  $j$  in feed, vapor, and degasified liquid, respectively.

$x$  = moles of  $H_2S$  reacting with  $OH^-$  in absorber per unit volume of alkali solution.

$z$  = valency of the alkali which reacts with the hydrogen sulfide gas.

$\tau$  =  $W/v$ , the mean residence time of the liquid in the absorber/reactor.

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