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# Gaseous Air Pollutants and its Environmental Effect-Emittedfrom the Tanning Industry at Hazaribagh, Bangladesh

Md. Abul Hashem, Md. Samsul Arefin and Abu Jor
*Department of Leather Engineering, Khulna University of Engineering & Technology (KUET), Khulna-9203, Bangladesh.*

***ABSTRACT :****This article has focused on gaseous air pollutants and its environmental effect-emitted from tanning industry during leather processing, especially in unhairing & liming, deliming, pickling and finishing operations in which hydrogen sulphide ($H_2S$), ammonia ($NH_3$), chlorine ($Cl_2$) and volatile organic compounds (VOCs) are emitted respectively at Hazaribagh, Dhaka, Bangladesh. The toxic hydrogen sulphide ($H_2S$) gas has negative effect at atmosphere by the process of photochemical reaction; it increases the greenhouse methane gas. In atmosphere, gaseous form of ammonia ($NH_3$) reacts with available acids and form their corresponding salts cause cloudiness and finally they return to earth surface by wet or dry deposition which effects on aquatic life. Workers in tanning industries are directly inhaled toxic chlorine gas suffers withvarious health complexities. Emission of VOCs isthe mostly formaldehyde and it is captured in photochemical oxidation by ozone as well as UV radiation. It's an important precursor of smog formation where it reacts with oxides of nitrogen (NOx) including peroxyacetyl nitrate (PAN); smog decreases the visibility in the urban area.*

***Keywords:*** *Tanning industry, Emission, Air pollutants, Hydrogen Sulphide, Ammonia, Chlorine, VOCs*

## I. INTRODUCTION

Worldwide raw hide or skin is the basic raw materials for the tanning industry.Raw hide/skin contains two types of proteins i) structural and ii) non-structural protein. The fibrous protein is known as collagen that is converted to leather by the process of tanning. Tanning involves the conversion of putrescible raw hide or skin to make finish leather where a series of chemical operations are required to hold several types of attributes. The non-fibrous proteins like albumins, globulins etc. have to remove by a series of chemical treatment and mechanical operations. Each and every chemical unit treatment as well as mechanical operation produces different types of solid waste, liquid waste and gaseous air pollutants and most of the tanningindustries discharge as green (without treating/filtering) to the environment.

Worldwide tanning industries are known as obnoxious for being producing high pollutants and environmental degradation. In Bangladesh tanning industry is one of the fast growing industry. There are about 220 leather industries in Bangladesh, 85% of them are located in the western part of capital city Dhaka[1] and others are scattered all over the country [2]. Since the last decades of industrialization, Bangladesh is facing the environmental degradation of river, Buriganga and other linked rivers due to receiving the discharged green solid and liquid wastes from the tanning industries [3]. The solid and liquid effluent comprised of decaying flesh, soluble proteins, fat, toxic chemicals, dissolved lime, suspended and dissolved solids, organic matters, dyestuffs and coloring pigments, heavy metals like chromium etc. [4]. Gaseous air pollutants hydrogen sulphide ($H_2S$), ammonia ($NH_3$), sulphur dioxide ($SO_2$), carbon dioxide ($CO_2$), fume of formic acid, chlorine ($Cl_2$), volatile organic compounds (VOCs) etc. are produced in different stages of leather processing which are directly merged to atmosphere [5]. Gaseous air pollutants are returned to the earth surface as acid rain or fog or mist which effect on aquatic life, vegetation as well as on human health.

Due to generation of high pollutants as well as causing environmental degradation tanning industries of Bangladesh has gained a negative image at the good-tempered society therefore facing a severe challenge to survive. However, it is one of the export earning sectors to strengthen the national economy of the country. The Export Promotion Bureau reported that in the fiscal year of 2013-14 Bangladesh earnedUS$1.29million from the leather sector. Besides, gradually demands of finished leather and fashionable leather products growing all over the world due to its comfortable and distinct properties.

Unfortunately, excluding one tannery (Apex Unit-2) none of the tanneries has an effluent treatment plant (ETP) in Bangladesh. In Bangladesh, per day hideor skins are estimated to be processed for leather production 240MT in which generating 8.47 million liters wastewater and 98MT solid wastes [6]. It is estimated that in Bangladesh during deliming operation yearly $3.5\times10^6$–$12.8\times10^6$ $m^3$ ammonia is produced where $2.2\times10^6$–$8.1\times10^6$ $m^3$ is directly merged to atmosphere and $1.3\times10^6$–$4.7\times10^6$ $m^3$ is mixed at pH 8.5–9.0 in wastewater [7]. In atmosphere ammonia reacts with available acids *i.e.* sulphuric acid, nitric acid and hydrochloric acid to form their corresponding salts causing cloudiness [8]. Ammonia once is discharged to atmosphere, it returns to the earth surface either as gaseous form or as an ammonium ion [9].

The objectives of this article are to symbolize the status of selective emitted air pollutants $H_2S$, $NH_3$, $Cl_2$ and VOCs from tanning industries, especially in unhairing & liming, deliming, pickling and finishing operations and their change in the atmosphere as well as effect on the environment.

## II. STUDY AREA

The area is located at Hazaribagh, in the western part of capital city Dhaka where most of the tanning industries situated and covering an area of 25 ha [2]. Every day leather processing starts normally at 6:00 am and continue until 10:00 pm. In some cases the operations continuously run whole night. During this long time, various chemical and mechanical operations are employed and each chemical unit operations are generating toxic gaseous pollutants which directly merge to atmosphere without any filtering. All these primary pollutants are changed by the atmospheric reaction produce secondary pollutants and finally causes harmful to the environment as well as effect on human health. The conventional leather processing flow chart of Bangladesh is shown in **Fig. 1** with emitted gaseous air pollutants.

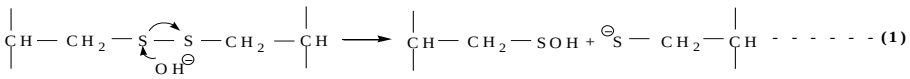
## III. MATERIALS AND METHODS

### *3.1 Data Collection*

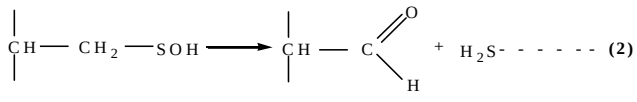
Conventional leather processing chemical unit operational steps was monitored to know the generation of gaseous air pollutants. Most of the tanning industries are used almost same chemicals for the same operations. Gaseous hydrogen sulphide ($H_2S$), ammonia ($NH_3$), chlorine ($Cl_2$) and volatile organic compounds (VOCs) are generated in unhairing & liming, deliming, pickling and finishing operations, respectively.

### *3.2 Unhairing &Liming*

In unhairing & liming, sodium sulphide ($Na_2S$) and calcium oxide (CaO) are used to remove keratinous and non-fibrous proteins. In some cases sodium hydrosulphide (NaSH) is also used instead of sodium sulphide. During liming operation gaseous hydrogen sulphide ($H_2S$) is produced which directly merges to atmosphere. At first the cystine is hydrolyzed in the presence of NaOH as reaction (1).




In the presence of sulphides competitive reaction hydrogen sulphide ($H_2S$) is produced as reaction (2).



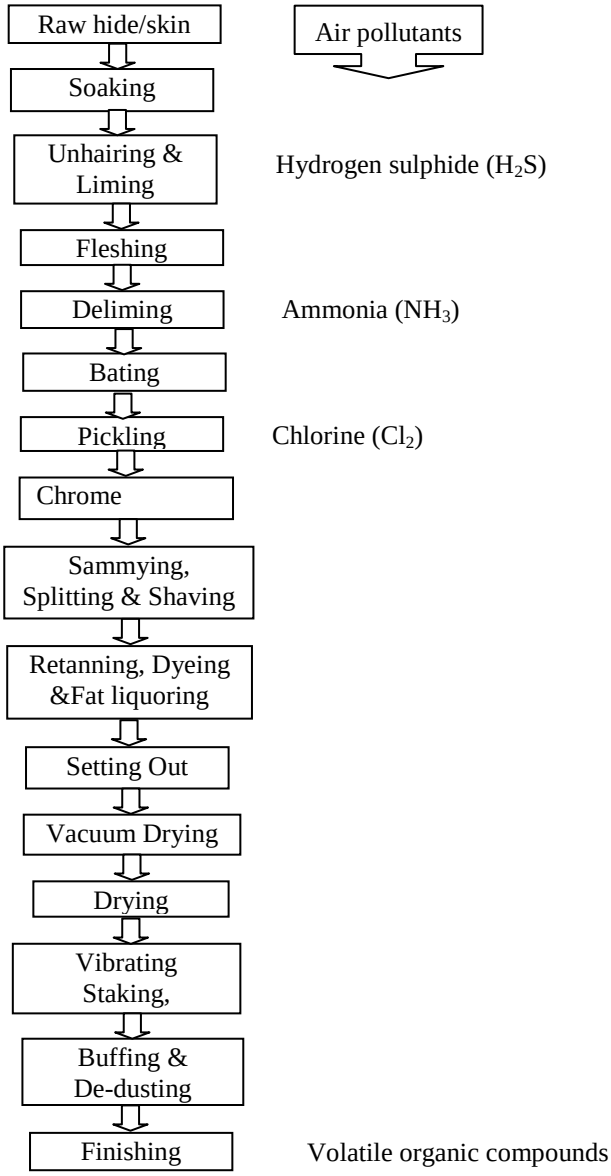



**Figure 1**. Flow chart of leather processing

### *3.3 Deliming*

After fleshing, subsequently limed pelt is passed through an operation to remove lime from the inside of pelt is known as deliming. During unhairing & liming operation different percentage of lime is used based on the hide/skin substances. The solubility of lime is 1.65 g/L at 20°C and with increasing temperature the solubility is decreased [10] that's why unhairing & liming operation is continued for long time 18-20 hrs. After unhairing & liming, pelt contains lime as per weight basis from 0.5–2.0% [11]; this lime has to be removed fully or partially before starting the next operation like bating. Normally lime is removed by neutralizing either acids, acid-salts, ammonium salts or other substances with an acid reaction. In Bangladesh only limited number of deliming agents are used like ammonium sulphate ($(NH_4)_2SO_4$) and ammonium chloride ($NH_4Cl$).

$$Ca(OH)_2 + NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O \text{ - - - - - - - - } (3)$$

$$Ca(OH)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_3 + 2H_2O \text{ - - - - - } (4)$$

It is clear from the equations (1) and (2) that ammonia is produced from the both deliming agents. The percentage of deliming agents ammonium sulphate and ammonium chloride are used depending on the lime

content in pelt. In the conventional deliming process sodium met-bisulphate ($Na_2S_2O_5$) is used to get the bleaching effect on pelt surface. The percentages of conventional deliming agents are used in tanning industries are shown in the **Table 1.**

**Table 1. Deliming agents are used at selected tanning industry**

| Tanning industry | % of Deliming agents | |
|---|---|---|
| (ID) | $NH_4Cl$ | $(NH_4)_2SO_4$ |
| T1 | 0.25–0.5 | 2.0–3.0 |
| T2 | 0.30–0.5 | 1.5–3.0 |
| T3 | 0.25–0.4 | 2.0–3.0 |

### *3.4 Pickling*

Immediately after deliming and bating, pelt is pickled (acidify) with strong acid usually sulphuric acid ($H_2SO_4$) together with organic acid (formic acid) to adjust pH 2.5–3.0 to facilitate the next operation such as chrome tanning. In pickling, sodium chloride (NaCl) and sodium chlorite ($NaClO_2$) is used. Sodium chloride (NaCl) is used to prevent the acid swelling and sodium chlorite ($NaClO_2$) is usedan oxidizing unhairing agent to split up the disulphide (−S−S−) bond. Sodium chlorite ($NaClO_2$) dissolves inaqueous formed chlorine dioxide ($ClO_2^-$) which reacts with keratin (cystine) formed keratinsulfonic acid and free chlorine [12]. This reaction is occurred in acidic condition and takes about 24 hrs. That's why after using oxidative unhairing agent drum usually keep stopped for overnight to complete the reaction [13] as well as pelt can easily uptake the acid into cross section level. During this long reaction time, produced chlorine gas is come out from inside the drum by hollow axle and directly merges to atmosphere.

$$\mathbf{ClO^- + H^+ \rightarrow 2ClO_2 + ClO_3^- + Cl^- + H_2O} \text{ - - - - - - - - - - - - (5)}$$

$$\mathbf{4R–S\text{-}S\text{-}R + 10ClO_2 + H_2O \rightarrow 8R{-}SO_3^- + H^+ + Cl_2} \text{ - - - - - (6)}$$

In the next morning sodium thiosulphate ($Na_2S_2O_3$) is introduced to decompose the excess $ClO_2$, in order to prevent oxidation of subsequently used as trivalent chromium (basic chromium sulphate)to hexavalent chromium.

### *3.5 Finishing Operations*

The last chemical operation of leather processing on dried leather surface to change its surface effect, both the aesthetic and functional aim is known as finishing. Different type of binders, mixture of pigments, dye solutions, waxes, fillers, and auxiliaries are applied on leather surface to make it attractive. After giving a final top layer on leather surface various fixing agents are used including formaldehyde, polyurethane, nitrocellulose etc. All these volatile reagents, spray dusts are emitted to atmosphere during finishing operation.

## IV. RESULTS AND DISCUSSIONS

### *4.1 Hydrogen Sulphide ($H_2S$) in Unhairing & Liming*

In tannery, normally unhairing & liming takes for about 18–20 hours; during long time chemical reaction as well as mechanical agitation produce $H_2S$ gas. The $H_2S$ gas comes out from the hollow axle of drum/from open paddle which is directly mixed with air inside the tanning industry. It is a colorless gas, and is slightly heavier than air. It has a strong odor of rotten eggs. In tannery, operators are used to work without nose mask and frequently inhale gaseous $H_2S$ and are suffering in difficulties. High concentration of $H_2S$ (> 900ppm) for one minute causes instant coma and death [14]. $H_2S$ is not only produced in liming but also produced when spent lime liquor is mixed with the acidic ranges spent tanning liquor like spent chrome tanning or spent pickle liquor. It is the conventional practice to discharge spent lime and chrome tanning liquor simultaneously at the same stream continuously $H_2S$ gas is produced. People in the tannery areas are inhaled the poisonous $H_2S$ gas. In 2010, three workers died of inhaling toxic $H_2S$ gas; it was produced by wrong dosing of chemicals mixing of basic chromium sulphate (BCS) in the liming drum at night. In next morning when workers opened the door of drum inhaled huge amount of $H_2S$ gas and cause death [15]. The fluxes of $H_2S$ led to toxic levels of $H_2S$ at atmosphere by the atmospheric photochemical reaction. Besides, ozone shield destroy and increase the greenhouse methane gas [16].

### *4.2 Ammonia ($NH_3$) in Deliming*

As of (1) and (2) equations, one part of calcium oxide (CaO) can be neutralized by 2.4 parts of ammonium sulpahte or 1.9 part of ammonium chloride. In both cases equivalent amount of gaseous ammonia is produced. As estimated, per day 220MT hides and skins are processed at Hazaribagh; after unhairing & liming pelt contains lime 1.2–4.4MT. To remove this large amount of lime by so called deliming operation, yearly $3.5\times10^6$–$12.8\times10^6$ $m^3$ ammonia is produced from the tanneries at Hazaribagh, Bangladesh. Usually, pH of deliming is kept 8.5–9.0 to aid the next operation known as bating. In this pH, solubility of ammonia in water at 25°C is 15.3%–36.6% [17]. Assuming that produced $1.3\times10^6$ – $4.7\times10^6$ $m^3$ of ammoniais directly discharged into wastewater at pH 8.5–9.0 and finally mixes to river, Buriganga; remaining $2.2\times10^6$ – $8.1\times10^6$ $m^3$ is merged directly to atmosphere.

Ammonia is a highly hydrophilic base and it has irritating properties. It affects on human being due to its alkaline corrosiveness; either it's gaseous or liquid form can be irritate to the eyes, respiratory tract and skin [18]. Ammonia and its hydroxide are corrosive, can rapidly penetrate to eye and may cause permanent injury.

In tanneries, operators are frequently handled the delimed pelt or leather and waste liquor with bare hands and foot as well as without nose mask. Besides, persons who are engaged other works are exposed to inhale gaseous form of ammonia from inside the tannery. Resulting, person who are directly or indirectly involved in the tanneries are getting contact with ammonia or its hydroxide are suffering from many difficulties.

Ammonia is lighter than air, as a result after emitting from any sources- it is directly merged to atmosphere. It has a short atmospheric lifetime of about 24 hrs. [19]. Once ammonia is emitted to atmosphere it could undergo conversion to $NH_4^+$ aerosol due to its highly reactive nature and quickly deposited near to the sources of emission [20]. The conversion of ammonia ($NH_3$) to ammonium ion ($NH_4^+$) in aerosol is dependence on the concentration of acids in atmosphere. Formed ammonium salts at atmosphere are the main components of smog aerosols; it effects on cloudiness of the atmosphere as well as earth radiation budget [8].

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \text{ - - - - (7)}$$

$$NH_3 + HCl \rightarrow NH_4NO_3 \text{ - - - - - (8)}$$

$$NH_3 + HCl \rightarrow NH_4Cl \text{ - - - - - - (9)}$$

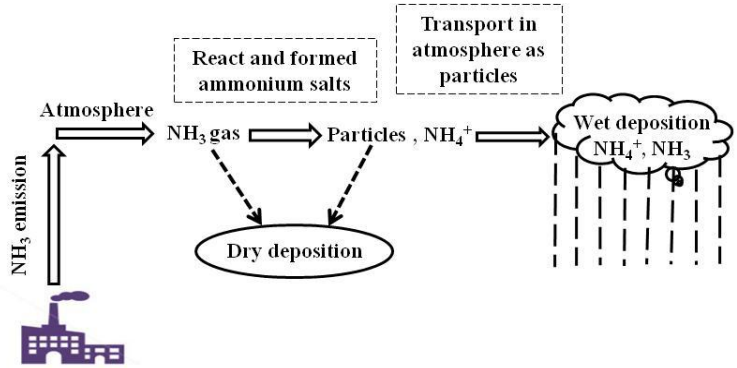



**Figure 3.** Emission of ammonia and its change at atmosphere

Gaseous ammonia or particulate matters can be removed from the atmosphere by wet and dry deposition and may occur: (i) as gaseous form (ii) in the aqueous form as ammonium ion ($NH_4^+$) and (iii) as an aerosol in submicron atmospheric water droplets. In the **Fig. 3** shows the emission of gaseous ammonia in the atmosphere and its changes. The ammonium ion associated with nitrate, sulphate or some other anion is incorporated into an aerosol or as part of the ionic mix is found in cloud and raindrops.

### *4.3 Chlorine ($Cl_2$) in pickling*

Gaseous chlorine ($Cl_2$) is produced in pickling which is responsible for atmospheric pollution. It is a toxic gas that irritates the respiratory system. It is 2.5 times heavier than air that's why produced gaseous chlorine in pickling remains inside the drum; workers are frequently inhaled toxic chlorine gas when they open the door of the drum. Person could loss of consciousness and possibility death if he/she trapped in high concentration of chlorine [21].

### *4.4 VOCs in finishing operations*

Volatile organic compounds (VOCs) are emitted in finishing operation including formaldehyde, acetone, butyl acetate, isopropyl alcohol etc. In tanneries operators are frequently handled organic solvents with bare hand and without nose mask; they are suffering in various difficulties like abdominal pain, diarrhoea, convulsion and respiratory problem. Although most of the developed countries have reduced the using of formaldehyde (H-CHO) as well set a permissible level in leather [22]. Tanneries of Bangladesh are also used formaldehyde and others organic solvents. Due to their high vapor pressure a good fraction is emitted to atmosphere during finishing operation; as formaldehyde is the precursor of many chemical compounds.

The VOCs are the atmospheric air pollutants. They are involved in photochemical oxidation by ozone as well as UV radiation [23]. The H-CHO emitted from the tanneries, it has short-lived and typical life-time is a few hours in day time [24]. The primary reaction of emitted formaldehyde in the air is direct photolysis and photo chemically produced hydroxyl radicals ($OH^{\cdot}$). *Atkinson* [25] reported that photolysis of formaldehyde occurs according to the following reactions:

$$H\text{-}CHO + h\nu \longrightarrow H_2 + CO_2$$

$$\longrightarrow H^{\cdot} + \dot{H}CO \quad ---(10)$$

Where, $h\nu$ represents energy. Formaldehyde reacts with hydroxyl radical and produce water and HCHO radical [25].

$$H\text{-}CHO + OH^{\cdot} \longrightarrow H^{\cdot} + \dot{H}CO \quad ---(11)$$

The above reaction and subsequently react with HCO radical may lead to the production of water, carbon monoxide, formic acid, and per hydroxyl radical or formaldehyde adducts [26]. Due to its high solubility transfer into rain and returns to earth surface water as wet deposition which may be important sinks [27]. In the urban atmosphere, formaldehyde is an important precursor in smog formation where it reacts with oxides of nitrogen (NOx) and other compounds like peroxyacetyl nitrate (PAN) [28] and smog decreases the visibility.

## V. CONCLUSION

In tanneries, various air pollutants $H_2S$, $NH_3$, $Cl_2$ and VOCs are produced; depending on their solubility a good fraction are directly merged to the atmosphere. Emission of $H_2S$ led to toxic levels of $H_2S$ at atmosphere by photochemical reaction resulting destroying ozone shield and increases the greenhouse methane gas. In the atmosphere gaseous form of ammonia reacts with available acids as well as form their corresponding salts cause cloudiness. Chlorine gas is harmful for workers. Emissions of VOCs have negative impact to environment; after emission it returns to earth surface as wet or dry deposition causes smog in urban area reduces the visibility. It has become a foremost responsibility of the concern authorities including owner of tanneries as well as the environmental authorities to control the emission of air pollutants to atmosphere for cleaner leather production.

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