

EMISSIONS OF HYDROCHLORIC ACID VAPORS GENERATED BY PICKLING PROCESS FROM COLD ROLLING MILL OF STEEL STRIPS

Anisoara CIOCAN

"Dunarea de Jos" University of Galati, 111, Domnească Street, 800201, Galați, Romania
e-mail: aciocan@ugal.ro

ABSTRACT

The most important pollutant emitted in the sector of pickling within a cold strip mill in an integrated steel mill are the hydrochloric acid vapors. This work presents the chemical reactions between the hydrochloric acid and iron oxides layers formed on the surface of the steel strip after the hot rolling process and it analyzes different areas of the pickling line as generators of acid vapors. The measurement values of hydrochloric acid vapors concentrations in the working atmosphere are correlated with the operational regimes and with occupational exposure limit values according to national legislation. Finally, solutions that can be applied to reduce emissions of hydrochloric acid vapor in the sector of analysis are presented.

KEYWORDS: steel strip, cold rolling, pickling, hydrochloric acid, pollution

1. Introduction

Cold rolling mill within an integrated steel mill is a complex technological line which is specialized in the manufacturing of low carbon steel bands or sheets. A cold-rolled sheet is a hot-rolled sheet that has been further processed through a pickle line, which is an acid bath that removes scaling from the surface of steel strips. Then it is successively passed through a rolling mill without reheating until the desired gauge, or the thickness and other physical properties have been achieved. Cold-rolling reduces gauge and hardens the steel and, when further processed through an annealing furnace and a temper mill, it improves uniformity, ductility and formability [1, 2].

The main operations related to cold rolling of steel bands are: pre-treatment to surface preparation (pickling) for improved the quality of cold rolled bands; trimming and oiling; cold rolling for reduction in thickness of steel products; degreasing and heat treatment (annealing) to get particular metallic, chemical or mechanical performances, required by customers.

All of these sub-processes are sources of pollutant emissions: hydrocarbons and decomposition products of lubricant oil; acid aerosols and fumes;

nitrogen oxides and carbon monoxide, polycyclic aromatic hydrocarbons etc. [3, 4]. This paper analyses the pickling process and acid vapors emissions. The common pickling processes are operated at temperatures that usually give rise to acid aerosols and fumes. Also Emissions of acid vapors may arise also from acid regeneration processes [5].

2. Generation of hydrochloric acid vapors at pickling of the hot rolled steel strips

Emissions of hydrochloric acid vapors from pickling of the hot rolled steel strips of an integrated steel mill come from multiple sources.

During the hot rolling of steel, oxygen from the atmosphere reacts with the iron in the surface of the steel to form an iron oxides crust. There is a mixture of iron oxides, practically disposed as three kinds of scale which differ in the temporal and local evolution. The primary, secondary, and tertiary scale is formed on the steel band surface within the hot rolling process.

The share of three layers in the crust is different for different temperatures, oxidation times and steel composition (Figure 1).

The presence of oxides or scale on the surface of the steel is harmful when the hot rolled steel strip is subjected to cold rolling process. To remove iron oxides or scale from the surface of strip steel in order

to obtain a clean surface are required mechanically and chemically treatments. Firstly, is applied the de-

scaling of the hot strip material into scale breaker (placed downstream to pickling installation).

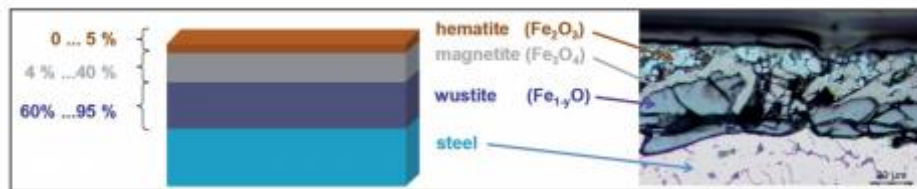


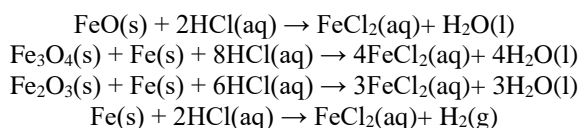
Fig. 1. Cross section of the three-layer steel oxide scale formed during the hot rolling stage on surface of the steel strip [6]

To increase the value of steel strip products it is essential to follow the second treatment. This involves the removing of oxides layers by the steel chemical pickling bath method (named pickling) [7, 8]. The steel strip is dipped in an acid bath (H_2SO_4 or HCl solutions). Such this is pickled for the removal of oxides and other residues from the surface. To dissolve iron oxides from the surface of a metal without any significant attack on the steel itself is used the HCl acid solution as pickle liquor. Hydrochloric acid pickling is widely used because has more advantages: high pickling efficiency; less pickling time; lower investments required; lower risk of embrittlement (hydrogen diffusion in the material), the process taking place at low temperatures; lower acid consumption per ton of pickled strip. However, sulphuric acid has a low vapor pressure and thus it requires less intensive ventilation. This is reflected in the cost-recycling regenerative technologies [1].

The HCl concentrations in a batch pickling process are 16.5 % for a fresh solution and 3.5 wt. % before acid replenishment. The rate of pickling increases with concentration of HCl and temperature.

The pickling line linked to tandem cold rolling mill is composed of several sections where take place specific technological operations: pickling in acid tanks with different concentrations, rinsing and dryer of steel strip.

In the acid tanks the iron oxides and metallic iron react with hydrochloric acid and ferrous chloride, water, and hydrogen gas are formed according to the following reactions [9]:



The hydrochloric acid pickling is carried out in heated bath. Usually the range of temperature recommended is 65...85 °C. Depending on the temperature of the pickling baths, the speed of passage of the strip through pickling baths is a maximum of 4 m/s. In these conditions HCl vapors are produced and released into the atmosphere during the pickling process (Figure 2).

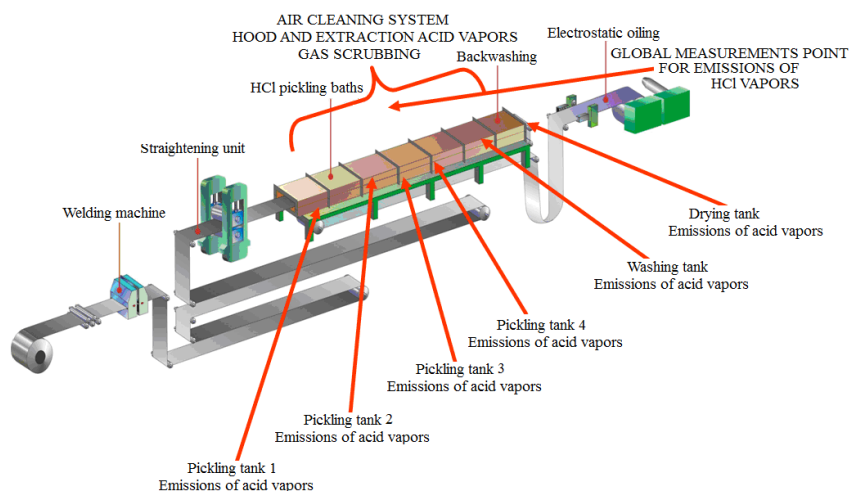


Fig. 2. Pickling line and hot points for producing and releasing of HCl vapours emissions

The HCl volatilized, together with steam and hydrogen gas, is released as acid fumes. It is present at the surface of the pickling tank and the pickled material. From here it is transferred to the rinse tank. Also it is present in chemical area of pumps and routes of acid.

In normal functioning and operation conditions of facilities from pickling sector hydrochloric acid vapors (as venting or fugitive emissions) are generally collected and treated in the air pollution control system to remove HCl.

There are some situations when emissions from many batch operations are uncontrolledly released as a hazardous air pollutant. Potential sources of HCl vapors are the loading and unloading operations (planned for maintenance or accidental stops). In this case the emissions of hydrochloric acid vapors are produced and released into atmosphere of the working hall as acid fumes. The natural circulation of air currents can get them up to tandem mill sector.

More emissions are released in the working space, damaging systems and equipment that handle and transport acid (pipelines, storage tanks, acid pumps etc.). In this case, emitted acid fumes in the, will be moved by the natural circulation of air currents.

The United States Environmental Protection Agency (EPA) specifies that for each million tons of steel processed at continuous coil or pushpull coil model facilities, storage tank losses are estimated to amount to 0.39 tpy. For other types of pickling

facilities, storage tank losses are estimated to be about 11.19 tpy of HCl per million tons of steel processed [10].

The recovery process of HCl from the waste pickling liquid in the acid regeneration process also can be a potential source of emitting significant amounts of hydrochloric acid vapors.

HCl emissions from processes of cleaning and acid regeneration depend on the pickling process used. A range of 1 – 145 mg/Nm³ maximum (up to 16 g/t) were reported; with the range reported by industry being 10 – < 30 mg/Nm³ (~ 0.26 g/t) [3].

3. Level of hydrochloric acid vapors in atmosphere of pickling sector

The concentration of hydrochloric acid vapors is periodically controlled in the hot points of the pickling line and in the area of the tandem mill. The Ministry of Health, the Institute of Public Health and the Medical Sciences Academy Bucharest specified procedures for the determination of hydrogen chloride emissions from stationary sources. A spectrophotometric method is used. The data collection frequency is once a quarter. The conditions of the data collection are: the pickling plant in operation; the pickling plant in stationary regime; with the pickling plant off (for maintenance works).

Table 1. gives the average annual values of measured concentration for HCl vapors.

Table 1. Average annual values of concentration of hydrochloric acid vapors for main sector of steel bands pickling lines and tandem mill, [ppm]

Measuring point	Year		
	2013	2014	2015
Tandem mill: rolling stands 1...5	0.20	0.22	0.20
Pickling sector: at steel strip dipping in the pickling bath	0.21	0.23	0.20
Pickling sector: acid tanks; dryer	5.90	6.20	5.80
Pickling sector: at steel strip extraction from pickling bath	0.61	0.62	0.60

The occupational exposure limit values for hydrochloric acid vapors generated in areas of steel

pickling lines imposed by Annex 1 from HG 1218/06.09.2006 are shown in Table 2 [11].

Table 2. Occupational exposure limit values for hydrochloric acid vapors generated by process steel pickling lines according to national legislation HG 1218/06.09.2006

Hazardous Air Pollutant	CAS	EINECS	Occupational exposure limit values			
			8 hours		short time duration (15 minutes)	
			mg/m ³	ppm	mg/m ³	ppm
HCl	7647-01-0	231-595-7	8	5	15	10

The level of measured concentrations in some areas of the pickling installation presented in Table 1 are compared with the occupational exposure limit

values presented in Table 2. The results are given in Figure 3.

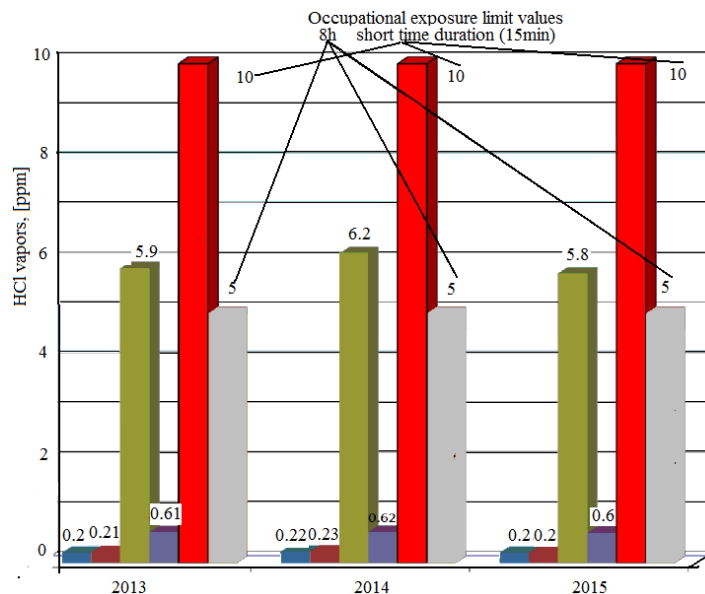


Fig. 3. Comparison between measured values and limits allowed by legislation for hydrochloric acid vapors in the working atmosphere

It is observed that the higher values of HCl vapors concentration were observed at the pickling tanks area. Also these are present in the area of the rinse tanks where are generated by the surface of the pickled steel band. Lower values were found at dipping and at the take out of steel strip. All measured values were below the limits stipulated by legislation

for hazardous pollutants. This demonstrates that the conditions of safety are respected.

The emissions from pickling line are collected and efficiently treated. The cleaning of exhaust gas and the ensuring of hydrochloric acid recuperation are imperatively used. The scrubber system to remove the hydrochloric acid vapors is shown in Figure 4.

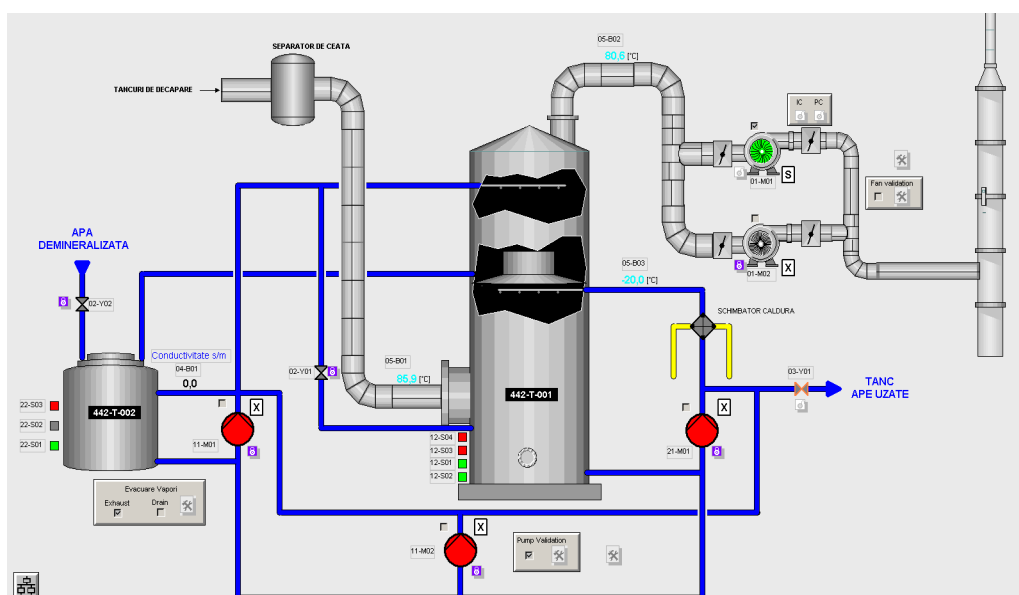


Fig. 4. Treatment facility for HCl vapors emissions

4. Conclusions

The acid emissions to air from cold rolling may arise from pickling and acid regeneration processes. With open pre-treatment systems, it is inevitable to eliminate the content of HCl vapor emissions in the air around the pickling facilities, especially when the material is taken out of the bath.

Generally, for all types of pickling sectors the emission control measures can be taken. The best solution for minimization of air emissions are: optimization of temperature, composition of pickle solution; covering of tanks; enclose pickling bath operations or install hoods and extraction systems; reduction of pickling emissions with gas scrubbing; pickling tank fume control [5].

To optimize operation of regeneration plant and the pickling section is necessary to minimize the acid losses as vapors. The measures to prevent emissions include a reduction of the waste gas volume and the contaminant load of the waste gas, which is exhausted from the pickling tanks.

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