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VERIFYING COMPLIANCE OF A METALLIC SURFACE TREATMENT COMPANY WITH BAT REQUIREMENTS, TO MINIMIZE EMISSIONS OF POLLUTANTS IN WATER

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Abstract
The main activity of the studied company is treatment and coating of metals (galvanizing plating), trapping and treatment of waste water. Galvanizing consists in creating a superficial diffusion layer of iron alloy.
BATs (Best Available Techniques) do not necessarily mean the most advanced technique available, but the best technique from an economic point of view for a particular installation.
Results of the research relate to compliance of the industrial water treatment plant to BAT best available techniques, in order to minimize pollutants discharged into the sewerage network. Furthermore, the current paper identifies possible dysfunctional problems of the galvanizing plant and of the sewage treatment plant and makes suggestions of remedies for possible technical and organizational problems.

Keywords: *BAT, metallic, pollution, surfaces, water*

Introduction

The analysed company is founded in 2003, specialized in the application of liquid paint on different aluminium, polyamide, ABS, polypropylene supports. The company has galvanizing, and also aluminium chrome plating and anodizing systems, painting systems and two water treatment plants.
The unit under analysis is located in the S-E part of Deva industrial area, about 500 m from European road 79 (Figure 1).
Lately, the company has grown, now also comprising a galvanizing hall. The decision to place a galvanizing line along with the sewage treatment plant was taken to diversify and broaden the range of surface treatments that the company offers against a background of rise of such surface treatments for the automotive industry.
The company's buildings are as follows: The administrative building; Galvanizing Hall; The Chroming Hall; Warehouse.
In the last period of time, the company has developed a treatment plant for the galvanizing line, which processes and treats the wastewater discharged from the processing line.
The galvanizing line is provided with a polyethylene cuvette treatment plant and a glass fibber decanter which takes up the flushing water from the line.
It should be noted that all of the station's vats have retention basins. The operation of the wastewater treatment plant is automatically controlled and any deviation from normal operating parameters is announced optically and audibly, immediately

leading to the automatic stopping of the wash water on the galvanizing line and, implicitly, on the line signalling. If the failure probes are not remedied, it is recommended to stop the chrome line. The access to the station control is made from the control panel, protected by a password to avoid any change of parameters made by someone other than the responsible person. Physical and chemical parameters of water are measured in real time, displayed and recorded.
Station operating principle: The wastewater treatment plant takes gravitationally the flushing water from the line and the mixing (gravitational and pumping) of the wastewater. The pickup storage takes place in storage tanks and the contents are dosed for pneumatic pump treatment.
Purified water is discharged into the sewerage network of Deva Town through a venture device that allows flow measurement and sampling for analysis.

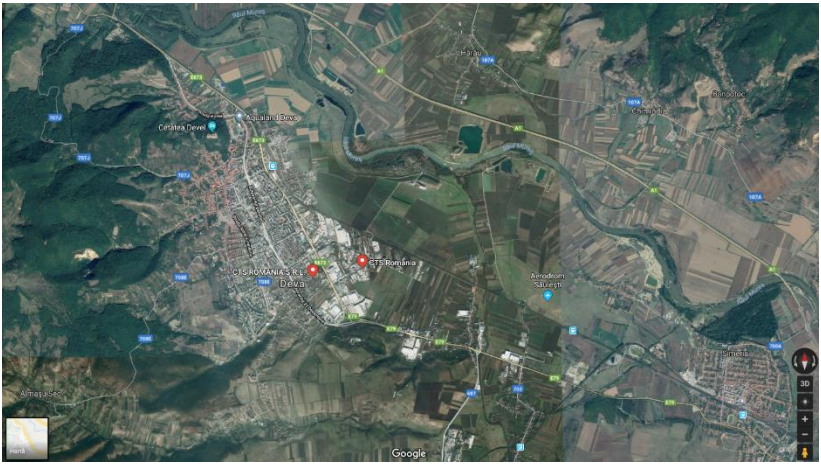

Figure 1. Location of the analysed company

Description of the galvanizing plant
Galvanizing of metal parts is a galvanizing operation, representing the electrochemical deposition of Zn^{2+} ions from the solution in the electrolysis bath on the surface of metal parts. This operation takes place in the line's active cuvettes, the rest of the vats being reserved for the rinses and operations that take place before and after galvanization. The technological process used by the company under analysis is one of the newest galvanizing methods. (Ord 818/2003 completed by Ord 1158/2005)
Galvanizing a metallic part has mainly three important steps:

1. *Preparing the part's surface before galvanization* - stage consisting of (chemical or electrolytic) degreasing the parts (with nitric acid 0.3 %), removal of metal oxide layer (pickling with 15-17% hydrochloric acid solution) naturally formed on the surface of raw parts and activation of the surfaces by immersion in a diluted acid solution;

2. Actual *zinc coating of raw parts by galvanization* - the process takes place in the acidic zinc-coating or alkaline-zinc coating tanks (active tanks). Each

active tank has 4 working positions allowing for zinc coating of 4 pieces at the same time; (SC EVALUARE IMPACT SRL, M 2016)

3. *Protecting and / or decorating the surface* of the parts after galvanizing, with decorative and protective purposes against further corrosion, achieved by:

• *yellow or blue deco passivation*, performed only after acidic galvanisation after a pre-activation of the surface in 0.3% nitric acid solution or in 10% hydrochloric acid solution.

• *black passivation* (alkaline galvanizing only) – optionally followed by varnishing for additional protection; between stages and operations, intermediate rinses and compressed air blowing are performed for partial drying. The final drying of the parts is carried out in the oven until all humidity is removed.

Operation of the galvanizing line is programmable, the part's supports are transported by 3 robots, the personnel being involved only in loading / unloading of the part's supports. In addition to automatic operation, robots can also be handled manually. The operation is based on cycles having a predetermined time (variable depending on selected range and computer adjustable), the parts generally spending an entire number of operating cycles in a particular cuvette. A running cycle lasts about 5 minutes and the total time that a piece spends on the galvanizing line is about 100 minutes.

The purification station for water resulting from technological processes of the galvanizing line is placed in the S-part of the galvanizing hall.

The treated water is discharged into the sewerage network of Deva City through a Venturi device that allows flow measurement and allows for sampling for analysis while regarding the GD 188/2002 with subsequent modifications, maximum admissible values.

The current paper describes the current situation of the site and highlights the pollutants and level of pollution as a result of the company's activity.

Methods of complying with BAT requirements and how to apply them to the galvanizing plant

In addition to national and international law, companies must verify compliance with European BATs in the field of each company. Thus, the company under review should consider whether it complies with requirements of the Best Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics 2006.

New open units must be designed to operate at levels similar to or superior to techniques in the reference documents. This depends on technical and economic capacity of each unit.

Although the documents do not establish a set of framework solutions, it nevertheless provides information on overall orientation of Member States as regards the levels to be achieved in the field of emissions and consumption of raw materials.

The purpose of these documents is also that best practice is regarded as a starting point for determining the current performance of existing installations or laying down requirements for new installations.

Recycling and recovery of wastewater, either during the process or when treating wastewater represents a BAT recommendation for Surface Treatment of Metals and Plastics 2006, to facilitate the recovery and reuse of substances, which is achieved at

the analysed company by industrial water treatment plants. (Wieszczycka K et all 2018)

BAT recommends the implementation of environmental management system and related procedures. In this respect, there are procedures for systematically reviewing, based on advances in the field, the raw materials used and suggestions of some more appropriate material, having a lower impact on the environment. The company has integrated the ISO 14001/2015 Environmental Management System.

According to BAT, the plant's facilities are continuously monitored on energy consumption, water consumption and raw material consumption, which allows for internal comparisons of monitored parameter values and for finding niches to reduce consumption. The data is recorded and analysed periodically by the technical service belonging to the analysed company.

According to BREF, generating free cyanide gas is avoided by separate storing of acids and cyanides.

There are hoods for aerosol suction at basic degreasing baths, acid pickling, activation, galvanizing plating.

Regarding compliance with BAT recommendations on efficient energy use, the Romanian company achieves the following:

- periodic metering of energy (monthly and annual);
- optimization of energy consumption, use of closed water circulation systems and verification of insulation status in pipelines and buildings;
- automation of technological processes;
- minimizing energy consumption of any type, maintaining and using the best available techniques for energy efficiency.

BATs associated with emission values are projected for samples of daily mixes. The emission levels associated with BAT are:

Parameter	Spills in the public sewerage (PRC) or surface water (AS) (mg/L)
Cr (VI)	0.1- 0.2
Cr total	0.1 – 2.0
Ni	0.2 – 2.0
Fe	
F	
Phosphate as P	
COD	
HC total	
VOX	

The company monitors effluents from the treatment plants and the results are compared with values set by GD 188/2002 (with subsequent modifications), namely: *Total Cr – 1.5 mg/L; Cr VI - 0.2 mg/L; Ni - 1.0 mg/L; Cu - 0.2 mg/L; Zn - 1.0 mg/L.*

Results and Discussion

Due to the fact that the analysed industrial platform is located on the Mures River Valley, 1 km away from it, in a flat area without obvious dishevelment, it is very unlikely that the studied site will affect the quality of Mures River. The only evacuated technological waters are discharged into the city's sewerage network. According to table 1, analysis results of waste water from the galvanizing line's

treatment plant are presented and compared with the admissible limit value set by Government Decision no. 188/2002 which includes NTPA-002/2002 normative regarding the conditions for evacuation of waste water in city sewerage networks.

Table 1. Analysis of discharged water from the galvanizing line's treatment plant

No.	Analysed indicators	Measure unit	Concentration values	Analysis method / reference document
1.	pH	upH	6.4(23.5°C)	SR ISO 10523/2012 PSL3 0510
2.	Suspension matter	mg/L	<5.0	SR EN 872/2005 PSL3 05-13
3.	Chemical oxygen consumption (COD)	mg/L	20.74	SR ISO 15705/2002 PSL3 01-04
4.	Biochemical oxygen consumption (BOD_5)	mg/L	6.8	SR EN 1899-1/2003/ PSL3 01-02
5.	Nitrites (NO_3^-)	mg/L	22.44	SR ISO 7890-3 / 2000 PSL 3 02-03
6.	Phosphates (PO_4^{3-})	mg/L	2.013	SR EN ISO 6878 / 2005 PSL 3 02-04
7.	Fluorides (electrochemical)	mg/L	<0.02	SR ISO 10359-1 /2001 PSL 3 03-14
8.	Chlorides (CI)	mg/L	69.28	SR ISO 9297/2001 PSL3 05-02
9.	Sulphates (SO_4^{2-})	mg/L	451.23	SUA Turbidimetric method 4500/1995
10.	Copper (Cu^{2+})	mg/L	0.11	STAS 7795-80; SR ISO 8288:2001
11.	Zinc $(Zn^2)^2$	mg/L	0.27	STAS 8314-87; SR ISO 8288:2001

Analysis of water in the treatment plant (Table 1) indicate some comments.

For pH, the value obtained is 6.4 upH, 0.1 upH lower than the limit value (6.5 ÷ 8.5 upH), indicating that the water discharged into the sewage is slightly acidic.

Suspended matter has values below allowed limits, of less than 5.0 mg/L, indicating that the treatment plant performs an efficient filtration of suspended matter.

Concentrations of oxidizable substances expressed as COD and BOD are well below allowed limits, indicating that there are few organic substances that decompose oxygen in the discharged water.

Concentrations of nitrates, phosphates, fluorides and chlorides are not standardized by GD no 188/2002 (with subsequent modifications), but the values are not problematical. The concentrations of sulphates are below maximum allowed limits, at about 75%.

Metal concentrations (Cu and Zn) are below the legal limits (maximum admissible limit for Cu = 0.2 mg/L and for Zn = 1.0 mg/L)

In conclusion, water discharged from the galvanizing line's treatment plant corresponds qualitatively, regarding the load with analysed indicators, resulting that pollution by these substances is insignificant.

The company under consideration falls under GD 188/2002 with subsequent modifications, on wastewater drainage conditions in the city sewerage networks, but also has to implement requirements of BATs.

The following shows the company's manner of complying with BAT requirements regarding waste water discharged into the sewerage network.

According to the Best Reference Document on Best Available Techniques for Surface Treatment of Metals and Plastics 2006, the Environmental Management System is very important, namely the environmental impact of the operation and eventual final shutdown of the installation - the development and use of cleaner technologies when it is feasible to regularly apply the sector-specific benchmarking system, including energy efficiency and energy saving, water efficiency and saving, raw material consumption and the choice of input materials, air emissions, water discharges and waste generation.
According to the Best Reference Document on Best Available Techniques for Surface Treatment of Metals and Plastics 2006, the Environmental Management System is very important, namely the environmental impact of the operation and possible final shutdown of the installation - development and use of cleaner technologies when it is feasible, to regularly apply the sector-specific benchmarking system, including energy efficiency and energy saving, water efficiency and saving, raw material consumption and the choice of input materials, air emissions, water discharges and waste generation.
It is also recommended to minimize the energy used to heat treatment solutions, optimize air intake and space heating. This is achieved by the studied company.
According to BAT recommendations, the selection of raw materials should observe:

- the use of quality chemicals (high purity);
- maintaining a detailed inventory of materials used on site;
- systematic replacement of raw materials and use of new, appropriate one having a low-impact on the environment.

The analysed company maintains a detailed inventory of materials used and the manner they are used in technological processes.
According to (BAT - Surface Treatment of Metals and Plastics 2006), the amount of water in the processes should be minimized by:

- monitoring all water and material consumption points within an installation,
- regular recording of consumption and control activity information;
- water recovery from rinsing solutions.

In table no. 2 is shows the most important BAT requirements and compliance type of the unit.

Table 2. BAT requirements and company action

Characteristic requirement of BAT	Answer
Confirm that a detailed inventory of raw materials used on site is maintained?	YES company makes an inventory of raw materials used on site
Compliance with environmental protection legislation	The monitoring of the environmental factors that are made on site is compared with the provisions of the legislation in force
BAT is the continuous optimization of input consumption (raw materials and utilities) relative to the reference values	The plant within the company is permanently monitored on energy consumption, water consumption and raw material consumption, which makes it possible to compare the internal comparison of monitored parameter values and to find consumption reduction niches. Data is recorded by the technical service

Avoid contamination of soils and waters by leakage or leakage of chemicals	The galvanizing line has a retention tank to avoid infiltration into the ground in case of accidental leakage
Avoiding or preventing the corrosion of storage containers, pipework, delivery systems and control systems by chemicals or corrosive fumes.	The solution tank are made of corrosion-resistant material and periodically checked for possible cracks or corrosion
Reducing water consumption by monitoring all water and material consumption points within an installation, regularly registering consumption and control information. The information is used to perform comparative analyses and the environmental management system	Within the Firm is implemented permanent monitoring of water consumption, for comparative analyses and for the environmental gestation system, and in the technological process is used the technological rinse by cascading rinse technique
Avoiding the need for rinsing between activities by using compatible chemicals (e.g., using the same acid pickling or activate the surface prior to treating the acid based coating).	The system is fully automated, and there is no need for rinsing between activities

The current company performs regular monitoring of water consumption and performs periodic checking of pipelines and buildings insulation status.
In the technological process, the analysed company does not achieve water recovery from rinsing solutions, and its use for other purposes (e.g., washing the yard). This will be implemented in the near future.
Also, according to BAT requirements, the company aims to extend the service life of solutions by keeping them within acceptable limits, by periodically filtering the solution. (Figoli 2017).

Conclusions

The paper describes the current situation and highlights water pollutants and the level of contamination as a result of the activity of the studied company, identifying the possibility of producing a major impact on the environment during operation of the galvanizing plant and if remediation works are needed. Reviews of previous and current data of the land and of activities carried out on the site, in order to present the manner of complying with requirements of prevention and mitigation of pollution according to national legislation, as well as the alignment to the best available techniques BAT, were mustered.
They were done measurements of water quality indicators discharged from the galvanizing line's treatment plant have been performed, showing that the discharged water frames within GD 188/2002 with subsequent modifications (NTPA-002/2002 normative), thus pollution by these substances is insignificant.
In addition to complying to national law, the company must also comply with requirements of BATs. According to the 2006 Best Available Techniques for the Surface Treatment of Metals and Plastics, the process water must be recycled and recovered, which is performed at the analysed company by the industrial wastewater treatment plants.

According to BAT, the plant's facilities are continuously monitored on energy consumption, water consumption and raw material consumption, which allows for internal comparisons of monitored parameter values and for finding niches to reduce consumption. Data is recorded and analysed periodically by the technical service belonging to the analysed company.

A non-compliance with BAT requirements was that the company under review did not achieve water recovery from rinsing solutions, and use for other purposes (e.g., washing the inner yard). This will be implemented in the near future.

This paper serves the competent environmental authority to identify data on the actual status of the site and is a benchmark against the previous situation. Also, this paper will enable the business owner to establish necessary steps to comply with the best available techniques in the field. Consequently, the measures to be applied are general, regarding good management, aiming at the supervision and maintenance of controlled levels of water quality.

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