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ENVIRONMENTAL EFFECTS OF TANNERY WASTE INCINERATION IN A TUNNEL FURNACE SYSTEM

EFEKTY ŚRODOWISKOWE PROCESU SPALANIA ODPADÓW GARBARSKICH W PIECU TUNELOWYM

Abstract: Processes applied commonly in the leather tanning industry pose a serious impact on the environment. Leather processing requires a substantial input of energy, water and chemicals. Moreover, it generates significant amounts of liquid and solid waste. Processing of 1 Mg raw hides gives up to 600-700 kg waste, the considerable amounts of which are solid tannery waste generated during or after the proper tanning process. Such waste contains chromium compounds, which are commonly used as tanning agents. Utilization of solid tannery waste is a severe problem for tanneries, the main method applied practically is landfilling. Solid tannery waste exhibits a relatively high heating value (approx. 12-14 MJ/kg), but also a considerable water content (for some types of waste up to 40-50%) as well as a chromium content reaching approx. 3%. Incineration of such waste is possible, it requires maintaining the proper process conditions in order to minimize the negative impact on the environment, however. The research was carried out using a prototype tunnel furnace designed especially for solid tannery waste incineration. The article presents a brief overview of the experimental installation and the research conditions as well as environmental effects of the process in the aspect of flue-gas composition, energy and mass balance, regarding particularly the chromium content in the process residues. As the research revealed, by the right process conditions setting it is possible to obtain chromium(III) oxide in the ash, which can be used as a chromium ore substitute in the chemical or metallurgical industry.

Keywords: tannery waste, tunnel furnace, waste incineration, chromium(III) oxide

Introduction

Processing of raw hides into leather is one of the oldest and most important industrial activity in the history of the mankind. It can be summarized as the conversion of raw hides or skins, which are prone to natural decay processes, into the stable and durable material, namely the leather [1]. Further on, the leather can be used for manufacturing a wide range of products. Through the ages the technology of tanning was changing, especially in the aspect of tanning agents which varied form urine to natural substances extracted from plants. The currently applied technology is based upon the process developed in the 19th century, in which chromium(III) salts are used as the tanning agents. Nowadays more than 90% tanneries worldwide apply chromium salts during the tanning process [1]. This technology allows to produce products of high quality, it brings about a severe burden for the environment, however. The leather production requires a significant input of energy, process water and chemicals. There is a huge amount of dangerous by-products generated as well, including wastewater (with high COD and inorganic salts concentration), solid waste and odours [1, 2]. Figure 1 presents the input/output overview of the process.

In recent years many developments have been presented in aspect of tannery wastewater treatment, including biological oxidation, membrane processes and others [3].

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One of the main problem for tanneries is the proper solid waste management, however. As presented in Figure 1, processing of 1 Mg rawhide generates up to 730 kg of solid waste. There are different types of such waste, depending on the operations, during which waste is generated. In many cases the only technology applied for waste treatment is landfilling, which has a negative impact on the environment [1, 2].

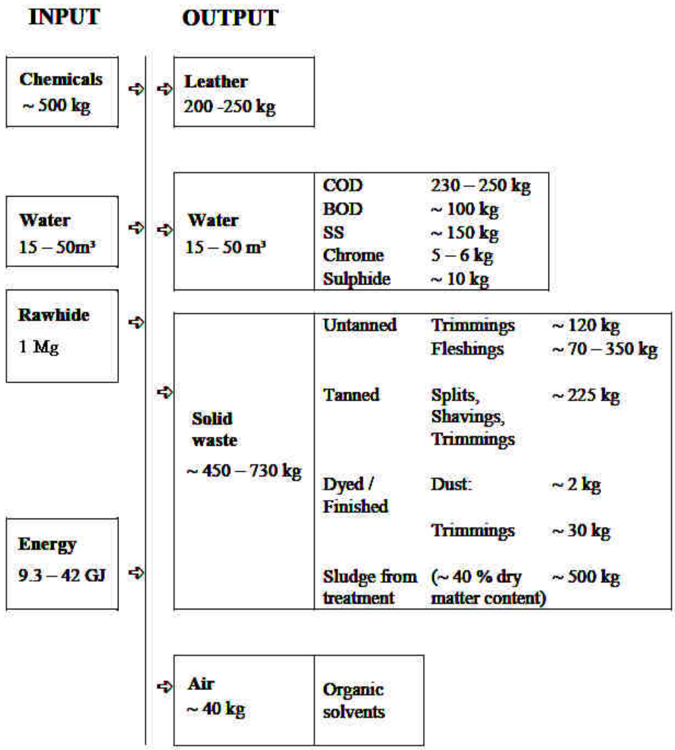

Fig. 1. Input/output overview for a conventional chrome-tanning process for bovine salted hides per 1 Mg of raw hide processed [4]

The main aim of this work was to present the technology of solid tannery waste incineration developed in cooperation with Faculty of Chemical Engineering and Technology, Krakow University of Technology, as well as to discuss the results of pilot tests and the environmental effects of the process.

Tannery waste

Types of tannery waste

The production of leather involves many single operations. The most important one is the proper tanning during which tanning agent compounds crosslink collagen fibres of hides. It assures the biological stability of the final product. In the group of operation prior to the proper tanning (knows as beamhouse operations) there are generated such types of waste as hide trimmings (unused pieces of hides) and fleshings (rest of the tissues scrapped mechanically off). They are biologically unstable and prone to decay processes. The types of waste generated during the operations conducted after the proper tanning, namely leather trimmings, splits, shavings and dust, are of the same biological stability as the leather itself, as they contain the same chromium compounds in their inner structure. Solid waste comes also form wastewater sludge [1, 2, 4, 5].

Amounts o tannery waste

As the FAO statistics reveal [6], the worldwide annual production of bovine hides and skins amounts to about 6 million Mg (wet salted weight) - see Table 1. Sheepskins, lambskins, goatskins and kidskins are processed for 600 thousand Mg (dry weight). It means that, roughly calculating, about 3.5-4.0 million Mg solid waste is generated annually. In Poland the production of bovine hides in recent years is stable and amounts to approx. 28 thousand Mg. Other sources give information on the amounts of leather produced in Poland - in years 2012 and 2013 it was 14.4 and 13.9 thousand Mg, respectively [7]. Based upon these values the amounts of solid tannery waste generated annually in Poland can be estimated giving not less than 15 thousand Mg waste.

Table 1

Production of bovine hides and skins (wet salted weight [thousand Mg]) [6]

	2001-2003 average	**2007**	**2010**	**2011**	**2012**	**2013**	**2014 (prel.)**
World	5 934.0	6 777.0	6 416.5	6 390.2	6 400.3	6 574.4	6 617.1
Europe	1 149.0	1 030.2	1 012.1	989.1	959.1	965.5	977.7
EU (27)	668.7*	702.2	700.6	699.2	670.3	668.2	669.3
Poland	30.7	24.6	26.6	33.8	28.3	28.2	28.3

* EU (15)

Characteristics of tannery waste

Tannery wastes consist mostly of organic matter, which indicates that its incineration is feasible. Table 2 presents the characteristics of tannery waste which is of importance in the aspect thermal treatment.

Table 2

Characteristics of tannery waste [5, 8]

Types of waste		**Lower heating value**	**Water content**	**Combustion residue - ash**	**Total organic substances content in dry matter**
		[kJ/kg]	**[%w/w]**	**[%w/w]**	**[%w/w]**
Untanned	Hide trimmings	7 753	59.9	4.7	86.9
	Fleshings	8 952	59.5	4.6	91.4
Tanned	Shavings	6 663	53.6	7.8	87.5
	Buffing dust	16 953	14.3	6.2	87.4
	Leather trimmings	19 772	10.2	4.7	87.7
Sludge		716	54.7	24.3	65.5

Worth noticing are: relatively high heating values, small amounts of inorganic matter (apart from sludge), as well as high water content rates in cases of some waste types, which implies the necessity of waste drying prior to the incineration process. The tanned waste (trimmings, shavings, dust) contains approx. 3-4% chromium, which comes from the proper tanning operation [1, 8].

Experimental

The installation

In [8] the concept of tannery waste incineration was described. The idea was to use a tunnel furnace system to enable the drying of waste in the first zone and assure proper conditions of combustion. In order to carry out research an experimental installation was built. In a tunnel furnace it is possible to maintain thermal conditions which continuously change along the length of the tunnel. It enables a virtual division of the tunnel into a few sections, in which successive processes take place: waste drying, volatilization of organic matter and combustion.

The system was manufactured by Firma Czylok, Poland. The tunnel is approx. 7 m long. The waste is put in special containers with perforated bottoms (to allow air circulation), which are transmitted through the tunnel by a roller system. Preheating and maintaining the temperature during the process is possible due to the three sections of electric heaters. The nominal power of the total system is 78 kW. The system is equipped with temperature, pressure and oxygen sensors, which give information about temperature at several points of the system, pressure at the entrance and in the combustion section, as well as oxygen concentration in the flue gas. The heat exchanger enables cooling the flue gas, which eventually goes out through a chimney equipped with measurements inlets for flue gas analyzers. The detailed information on the system can be found in [7].

Flue gas analysing

In order to measure the concentration of contaminants in the flue gas following instruments were applied:

- AWE-PW analyzer (producer, ZAM Kety sp. z o.o., Poland) for analysis of VOC concentration in the flue gas;
- Ecom-Sg Plus analyzer (producer: rbr Computertechnik GmbH, Germany) for measurements of SO_2, NO, NO_2 and CO in the flue gas;
- P-10ZA analyzer (producer, ZAM Kety sp. z o.o., Poland) for the determination of flue-ash concentration in the flue gas.

Process conditions

There is a wide range of process conditions settings, which vary depending on types and amounts of waste processed, amounts of process air, temperatures in the successive zones of the tunnel, process air temperature, velocity of transmitting containers with waste along the tunnel, etc. For the purpose of the aim of this work such parameters were set which enable the stable and controllable work of the installation. It was possible due to long period of initial tests which helped the staff to learn how the process varies depending on changes of the input parameters.

The incinerated waste was: leather trimmings, shavings and buffing dust, mixed together, in a weight ratio of 2:2:1. The average heating value of the mixture was approx. 13 900 kJ/kg, the average water content - approx. 28% w/w. Each container consisted 3 kg (±0.1 kg) of the waste mixture. In one series of experiment about 27-30 containers of waste were submitted to the process (approx. 81-90 kg). The waste flow was 15 kg/h (5 containers in an hour), which gives 12 min of time interval between the introduction of successive containers. The temperature of the preheated process air was 350ºC. The air was introduced right after the entrance door of the tunnel. The temperature in the combustion section was set at 875ºC in order to exceed 850ºC - the minimum temperature of waste incineration allowed by EU regulations [9]. The introduction of containers started when the temperature in the combustion section approached 650ºC. The total time of container transmission through the tunnel was 1 h 45 min. The temperatures, pressures, and oxygen content in the flue gas were recorded.

Results

As the result of the process the waste was incinerated. The residues were flue gas and ash. After the initial time of stabilizing the temperature in the tunnel it reached the level of 860-870ºC in the combustion section of the tunnel. The temperature changes along the tunnel are periodic and correspond to the introduction and ignition of successive portions of waste.

Process balancing

In order to describe environmental effects the energy input/output ratio as well as mass fluxes have to be known. The balance was calculated for 1 hour of incineration process in the most stable conditions which could be obtained during the experiment.

Mass balance

To calculate the input mass fluxes the waste as well as the process air were taken into consideration. The average composition of tannery waste as given in [2, 10] enabled to calculate the fluxes of C, N, O, S, H and inorganic compounds in the waste. The mass flux of air was calculated thanks to indications of volume flux measurements enabled by the measurement equipments installed in the experimental tunnel furnace system.

To calculate the output mass fluxes, the ash and the flue gas were taken into consideration. According to ash analysis the dry ash contains 56.4% w/w chromium [5]. This allows to establish the mass flux of chromium in the output. The mass fluxes of flue gas components were either calculated based on the input mass fluxes (nitrogen mass flux), combustion stechiometry (carbon dioxide and water mass fluxes) or analyzes carried out during the process (oxygen and contaminants mass fluxes). The average concentration of contaminants is shown in Table 3. The details on the calculating procedure are presented in [5]. The mass balance of the tannery waste incineration process are presented in Table 4. There is a slight difference in input and output values which undoubtfully is related to measurements errors and is negligible.

Table 3

Concentrations* and mass fluxes of measured contaminants in the flue gas

Contaminant	Average concentration [mg/m^3]	Mass flux [g/h]
VOC	10.7	2.53
Flue-ash	69.5	16.4
SO_2	753.2	178.1
NO_x	502.1	118.7
CO	296.4	70.1
Sum		385.8

* in the process conditions, without reference to standardized oxygen concentration in the flue gas

Table 4

Mass balance of the tannery waste incineration process [kg/h]

	Input		Output	
	1. Waste	**15.0**	**1. Ash**	**1.10**
	• Water	4.20	• Chromium in ash	0.62
	• Carbon	5.08	**2. Flue gas**	**302.0**
	• Nitrogen	1.51	• Nitrogen	218.5
	• Sulphur	0.10	• Carbon dioxide	18.6
	• Hydrogen	0.65	• Water	12.85
	• Mineral content	1.08	• Oxygen	51.7
	• Chromium	0.59	• Contaminants	0.39
	2. Combustion air mass flux	**287.7**		
	• Water	2.8		
	• Nitrogen	218.5		
	• Oxygen	66.4		
Sum		**302.7**		**303.1**

Energy balance

The energy fluxes which enter the system are: chemical energy of the waste and electrical energy required by the installation to maintain the appropriate temperature in the combustion section and to drive rollers, fans and other system elements. To assess the output fluxes the energy exchanged in the heat exchanger as well as energy losses in the flue-gas and in form of heat radiation have to be taken into consideration.

Electrical energy consumption and the energy flux exchanged in the heat exchanger are recorder by the installation controller. The energy flux which enters the system with the waste (chemical energy) was calculated on the basis of heating value. The values are presented in the Table 5. It has to be emphasised that due to the technical limitations (necessity to use electrical heaters instead of preferable gas burners, inability to increase heat recovery rate in a given heat exchange system) the efficiency rate is low (21%). The calculations were presented here in order to give the complete overview of the process. They show that more than 100 kW is lost or partially accumulated in the furnace walls. The low efficiency rate is an important indication for the further upgrading of the system into the full-scale.

Table 5

Energy fluxes input/output overview

Flux type	**Value**
	[kW]
Input	
Chemical energy flux (in waste)	57.9
Electrical energy flux	74.0
Sum	131.9
Output	
Exchanged heat flux	28.0

Environmental effects of the process

To describe the impact of the tannery waste incineration process on the environment one important aspect has to be take into account, namely the comparison of the presented treatment method with the one applied so far. The waste used in the research were bound to be landfilled as landfilling is the most commonly applied treatment method for such waste in Poland [1].

Tannery waste landfilling requires minimal energy input as the disposal yards are most commonly located on the sites of tanning facilities. In most cases, there are no or little safety measures to protect the sites from emitting substances into ground waters (leaching through atmospheric fall) or atmosphere (odours, dust emissions). The main risk is connected with probability of chromium extraction from waste into environment, especially through leaching. Solubility of chromium(III) compounds, which predominate in tanned leather and leather waste, is very slight, but still possible. The pH is of importance - in the slightly basic conditions a redox reactions may take place, giving as a result much more soluble chromium(VI) compounds. Furthermore, organic matter originated form hide material processing is effective in forming soluble organic Cr(III) complexes [11, 12]. In case of uncontrolled chromium extraction from waste to I or II class surface waters for each single Mg waste approx. 10^4 m^3 water may become polluted (meaning the chromium concentration exceed 0.05 mg/dm^3 [13]). For this rough calculations the extraction rate on the level of 3-5% was assumed. The environmental effect of tannery waste landfilling is therefore definitely negative, unless precautions have been taken to ensure the proper bottom and cover sealing of the landfill site.

The presented incineration method for tannery waste treatment affects the environment mainly in two fields. The first effect comes form that fact that the technology generates waste itself, namely the flue-gas and the ash. Both residues contains contaminants which may affect negatively the environment.

In case of the ash it is noticeable that this residue amounts to less than 1/10 of the waste input mass and that it consist mostly of chromium(III) compounds. As the preliminary tests reveals [5, 8], the process temperature is too low for the chromium oxidation to take place, so nearly all chromium in the ash is the chromium(III). With relatively simple means it is possible not only to collect the ash in an environmental safe way, but also to reuse the ash in such applications, which require high chromium(III) concentration. It could be the chemical industry (production of sodium chromate(VI), the basic chromium substrate for a wide range of industrial processes) or metallurgy (the ash as a substitute of chromite ore for stainless steel production).

The emission to atmosphere includes carbon dioxide and contaminants. The analyzes of the basic gaseous contaminants show that there is a need for the flue gas cleaning system to be installed in the case of implementing the technology to industrial applications. This means additional costs and also waste generated during the flue gas cleaning (collected ash, absorbed sulphur compounds, etc.).

The second aspect of the process contributing to its environmental impact is the energy consumption. As the rough calculations show the energy uptake is too high in comparison to the energy reused. The low heat exchange rate, lack of gas burners (instead electrical preheating system was applied), as well as the long period of heat accumulation in the tunnel walls were these factors which lowered the energy efficiency of the whole system. In the optimal case, it should be possible to regain energy from the process, which would limit the negative environmental impact. As the experiments show, the additional energy input (apart from the chemical energy of the waste) can be significant and has to be taken into consideration.

Conclusions

Without full data on costs, emissions factors and energy uptake the comparison between waste incineration process in a tunnel furnace system and waste landfilling, which in most cases takes place so far, could be only qualitative. Even facing the fact that the incineration process requires some energy input and gives out emission of the substances which are not neutral to the environment, tanned waste landfilling seems to pose more potential threat to the environment components (ground and surface water, soil and living organisms) than any thermal treatment technology, mostly due to the risk of chromium penetration outside the waste disposal sites. The technology of tannery waste incineration presented in this paper is an attempt to develop such treatment method which would be implementable in industrial practise and safe to the environment. The research so far proved that incineration of tanned waste is possible, the tunnel system can be applied for such a process and that the combustion is complete, leaving no or little organic matter in the ash, which can be treated as the chromium concentrate to various applications.

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EFEKTY ŚRODOWISKOWE PROCESU SPALANIA ODPADÓW GARBARSKICH W PIECU TUNELOWYM

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Abstrakt: Stosowane powszechnie w przemyśle garbarskim technologie garbowania i wyprawy skór są istotnym obciążeniem dla środowiska. Procesy te wymagają znacznych nakładów energii, wody oraz chemikaliów, powstają również duże ilości odpadów, zarówno stałych, jak i ciekłych. Szacuje się, że podczas procesu obróbki 1 Mg skór surowych garbarnia generuje ok. 600-700 kg odpadów. Znaczna część tych odpadów to odpady stałe, powstałe podczas lub po procesie garbowania właściwego, dlatego też zawierają w swoim składzie związki chromu, stosowane powszechnie jako garbnik. Unieszkodliwianie tych odpadów jest dla garbarni uciążliwe, najczęściej są one składowane na przyzakładowych składowiskach. Stałe odpady garbarskie charakteryzują się stosunkowo wysoką wartością opałową (ok. 12-14 MJ/kg), ale też znaczną zawartością wilgoci (dla niektórych rodzajów odpadów nawet do 40-50%) oraz udziałem chromu wynoszącym ok. 3%. Unieszkodliwianie tych odpadów poprzez ich spalanie jest możliwe, wymaga jednak zachowania odpowiednich warunków prowadzenia procesu, by nie stwarzać zagrożenia dla środowiska. Badania prowadzono z wykorzystaniem prototypowego pieca tunelowego zaprojektowanego do prowadzenia procesu termicznego unieszkodliwiania odpadów garbarskich. W artykule przedstawiono krótką charakterystykę instalacji, przebieg badań oraz efekty środowiskowe procesu spalania odpadów garbarskich w aspekcie składu gazów odlotowych, bilansu energetycznego oraz bilansu masowego dla procesu ze szczególnym uwzględnieniem zawartości chromu w pozostałościach poprocesowych.

Jak wykazały badania, przy odpowiednim doborze parametrów procesu chrom występuje w popiołach w postaci tlenku chromu(III), możliwe jest więc ich wykorzystanie jako substytutu rud chromowych w procesach chemicznych czy metalurgicznych.

Słowa kluczowe: odpady garbarskie, piec tunelowy, spalanie odpadów, tlenek chromu(III)