1

Waste Management and Treatment of Residues in the Leather-Tanning Industry

Karl E. Lorber
University of Leoben, Austria

1. Introduction

During the so-called shaving process, where the Grain leather is brought to an uniform thickness, shavings are formed. When glutardialdehyde is used in chrome-free tanning, wet white pelts are produced and the remaining solid wastes from shaving are now called **wet white shavings**. About 100÷184 kilogram per ton of wet salted hide (kg/t_{WSH}) wet white shavings are generated in the tanning process, which corresponds to about 12÷20% of the total solid waste remaining in the tannery. In tannery waste management, utilisation as well as disposal is applied for this organic residue. Using anaerobic or aerobic treatment, biogas or compost can be produced, and combustion as well as landfilling may be employed for disposal. In many countries like Austria, direct landfilling is or was the main waste disposal pathway for wet-white shavings.

Due to new regulations (Landfill Ordinance 1996) in Austria and other European countries this will not be possible anymore from 2004 onwards, as the TOC-value (total organic carbon content) for waste to be landfilled is limited to TOC <5% only.

Moreover, **wet blue shavings** remain as residue, when the Grain leather from chromium tanning is brought to an uniform thickness. About 120 kg/t_{WSH} of wet blue shavings and wet blue trimmings with a Cr_2O_3 concentration of $1.7\%_{d.m.}$ and a water content of ca. 55% are generated, resulting in a total chromium load of 0.63 kg Cr/t_{WSH}. Buffing dust from the polishing of wet blue pelts also contains chromium but may be neglected due to its low quantity generated per t_{WSH}. Another source for chromium containing tannery waste is the sewage sludge from the waste water treatment plant, and when Cr is precipitated with $Ca(OH)_2$.

Looking at the existing waste management options for chromium containing wastes, it is interesting that so far no practical solution has been found which is real satisfactory. Prevention is possible only to a certain extent, because chrome-free tanning is not feasible for all types of leather (e.g. shoe leather production). Recycling of chromium by Cr-extraction from shavings and trimmings is not done for economical reasons and the direct utilisation of shavings and trimmings for LEFA-production is limited only and depends on the market situation. Biological treatment (composting) is useless because the toxic element chromium remains in the product, and landfilling is not a sound solution for environment at all, due to the Cr and TOC content of the waste materials. So there seems to be a real bottleneck in waste management of chromium containing tannery waste at present.

In this contribution, two aspects have been investigated. First, as wet white shavings do not contain hazardous compounds like chromium, utilisation is a promising alternative to landfilling. The aerobic treatment of wet white shavings for producing compost was investigated, because this method is simple and less costly compared to anaerobic reactor treatment for biogas generation. Therefore, it should be more suitable for developing countries. Secondly, an alternative approach is tried by thermal treatment and utilisation of wet blue shavings in brick industry. The idea behind is the immobilisation of chromium in a ceramic product. Hitherto, organic material (e.g. fibre sludge from pulp & paper industry) is applied for brick-making as an additive to build up pores, which are necessary to give the required properties (e.g. insulation) to the brick.

2. Aerobic treatment of wet-white shavings

2.1. Materials and methods

Compared to other tannery wastes like green fleshings lime, fleshings or lime split, "wet white shavings" is a more easy to handle material which is dry, does not emit bad odor and which does not attract pests and insects too much. Thus open windrow composting was used, in connection with turning of material for natural aeration.

For the experiments and trials reported below, altogether 16,280 kg of wet white shavings supplied by Tannery Vogel (Austria), have been used. This corresponds to a volume of about 37 m^3. The open windrows were of classical triangle shape with the dimensions: length: 8 m x width: 3 m x height: 1.5 m.

Turning of composting material for aeration was accomplished twice a week, using the facilities of the mechanical-biological treatment (MBT)-plant for household waste in Allerheiligen, Austria. To control and monitor the composting process, the moisture content of the composting material in the windows was kept between 40÷60% and the temperature inside the heaps as well as the ambient temperature was measured daily. The specific problem in composting tannery wastes like wet white shavings is the high nitrogen content of the organic material, which is about 14% d.m., resulting in an extremely low **C:N ratio** of **3÷3.5** only. This is far away from the optimum C:N ratio for composting, which is in the range between **C:N = 30÷35**.

In this case, an easily available carbon source with small content of nitrogen only must be added, to avoid excessive ammonia emissions caused by the microorganism and to keep the composting period (process time) within reasonable times (i.e. 15÷20 weeks). Hence the goal was to find adequate, C-rich amendment materials as well as the right mixture of wet white shavings (as N-source), amendment materials (as C-source) and bulking material (as supplier of pores and intermediate space for aeration). As composting of wet white shavings in developing countries mainly will be done at the tannery site and not in (municipal) waste treatment facilities or plants, the necessary C:N-ratio should be kept as low as possible to avoid the excess addition of C-rich amendment materials which may not be available at the place of a tannery. Considering these contraints, the following experimental set ups were chosen for the 4 trials described in Table 1.

The chemical and physical characterisation of the input materials used in the trials for composting are shown in Table 2.

In Fig. 1 the resulting C:N-ratio of the composting material (input) is shown, when different portions (% wet and % dry basis) of various amendments are added to the wet white shavings.

2.2. Experimental Results

A good indicator for the progress of the composting process is the development of the temperature inside the windrow heaps over the composting time. The temperature graphs measured for trial #1÷#4 are shown in Fig. 2.

Table 1. Material composition of composting mixtures investigated in trials #1÷#4
Tabela 1. Skład mieszanin kompostowanych w próbach 1÷4

Trial	Composting Mixture	Bulk density	Mass (Input)		Volume (Input)		C:N-Ratio
		[kg/m^3]	[kg]	[%]	[m^3]	[%]	
Trial #1	W.W. shavings	440	4,560	75	10.4	60	3.2
	straw	225	1,520	25	6.8	40	47.3
	Total:	353	6,080 kg	100	17.2 m^3	100	5.0
Trial #2	W.W. shavings	440	4,480	62	10.2	54	3.2
	stable bed straw	320	2,800	38	8.75	46	27.8
	Total	384	7,280 kg	100	18.95 m^3	100	4.3
Trial #3	W.W. shavings	440	3,420	31	7.7	42	3.2
	bio waste *)	700	7,560	69	10.8	58	18.8
	Total	594	10,980 kg	100	18.5 m^3	100	6.6
Trial #4	W.W. shavings	440	3,820	35	8.7	41	3.2
	sewage sludge	850	1,320	12	1.6	8	3.2
	bulking material**)	550	5,920	53	10.8	51	16.6
	Total	524	11,060 kg	100	21.1 m^3	100	6.2

*) *biowaste from separate household waste collection was used, already pretreated in the MBT-plant for 2 weeks*
**) *sieve residues (>12 mm and >24 mm sieve overflow from compost sieving in MBT-plant was used.*

Table 2. Chemical and physical characterisation of input material
Tabela 2. Chemiczna i fizyczna charakterystyka materiału wejściowego

Parameter	**Unit**	**Measured values**					
		W.W. shavings	**Straw**	**Stable bed Straw**	**Biowaste**	**Sewage Sludge**	**Bulking Material**
pH	-	4.03	6.92	6.79	7.03	7.07	7.19
eL	mS/m	3.37	2.27	3.78	4.64	2.36	3.36
ADR	mg/kg d.m.	8,145	2,795	5,610	1,490	1,330	2,615
Pb	mg/kg d.m.	<5	<5	<5	21.50	28.85	36.11
Cd	mg/kg d.m.	<0.5	<0.5	<0.5	<0.5	1.68	<0.5
Cr	mg/kg d.m.	22.14	22.32	19.87	88.97	184.1	156.2
Cu	mg/kg d.m.	6.05	6.32	11.77	32.59	155.0	39.36
Hg	mg/kg d.m.	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Zn	mg/kg d.m.	<125	<125	<125	137.4	1,019	400.2
TOC	mg/kg d.m. (%)	373,000 (37.3%)	261,000 (26.1%)	361,000 (36.1%)	286,000 (28.6%)	248,000 (24.8%)	200,000 (20.0%)
WG	%	56.40	16.02	69.9	57.70	73.24	32.49
GV	%	97.26	95.72	88.35	70.95	56.35	49.50
K	mg/kg d.m.	1,437	3,898	10,407	9,122	8,763	10,833
Cl	mg/kg d.m.	10,764	1,558	5,662	4,324	1,293	7,529
S	mg/kg d.m.	6,930	490	1,540	1,607	5,297	1,858
C	% d.m.	46.6	44.9	42.3	35.5	27.1	28.2
N	% d.m.	14.5	0.95	1.52	1.89	3.56	1.66
H	% d.m.	6.10	5.83	5.17	4.31	3.95	3.07
P	mg/kg d.m.	68.9	51.4	2,563	3,237	33,600	4,405

d.m: based on dry material

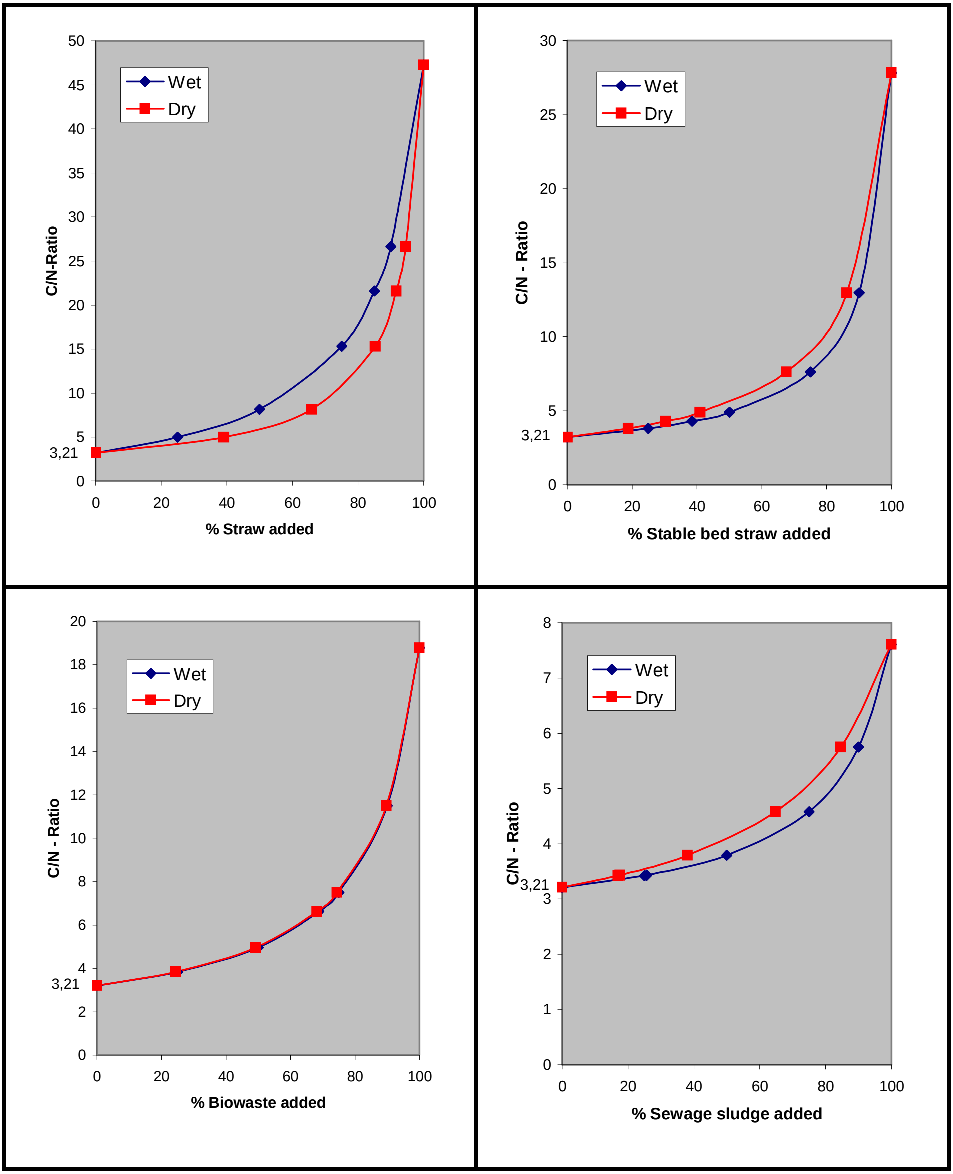

Fig. 1. C:N-ratio of composting material, when wet-white shavings are mixed with different amounts of amendments

Rys. 1. Stosunek C:N kompostowanego materiału, gdy białe wilgotne ścinki mieszane z różnymi ilościami dodatków

From Fig. 2 it becomes evident, that up to day 70, the aerobic process remains in the thermophilic phase with inside temperatures between 65÷50°C. Also after 120 days (i.e. more than 17 weeks) the composting process was not finished yet. Due to the low C:N-ratio of the mixture (C/N = 5), ammonia (NH_3) was developed and heavy odors could be traced around the composting heap. The amendment "straw" turned out to be a carbon source which is not easily available for the microorganism and it did decompose only slowly. As a practical result, Trial #1 was not successful.

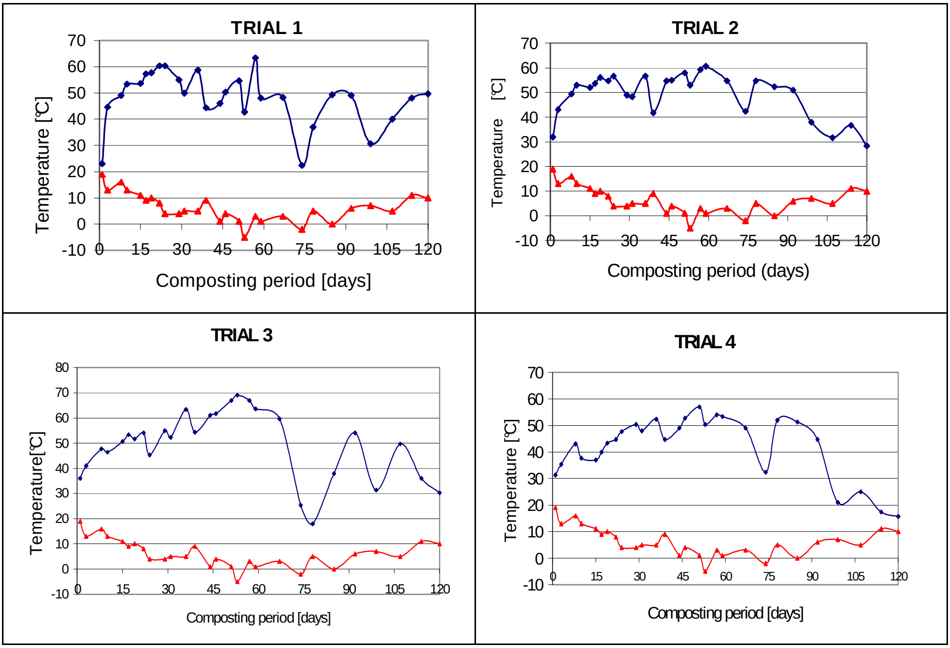

Fig. 2. Temperature development of composting process for trials 1÷4.
υ temperature inside heap, σ ambient temperature

Rys. 2. Zmiany temperatury w trakcie kompostowania w próbach 1÷4
υ temperatura wewnątrz pryzmy, σ temperatura powietrza

For Trial 2, it is shown that after a short lag-phase, the thermophilic phase is reached, which lasts up to day 90. Even after 120 days, the temperature inside the heap is 20°C higher than ambient temperature, indicating that the composting process is not finished because of the unfavourable C/N-ratio of 4.3. Once again, strong odors of ammonia and sulfur compounds were emitted from the heap.

Also Trial 3 turned out to be not really successful, as far as the duration of the rotting time is concerned. The thermophilic phase again was reached very soon and resulted in high temperatures over 70°C. On day 70, mesophilic phase was reached and continued up to the end of the trial. Once again, the C/N-ratio of 6.6 definitely was to low for a smooth rotting process, resulting in unreasonable process time and heavy odors of ammonia.

Compared to the composting experiments previously discussed, Trial #4 showed the best results in terms of temperature development of the process. After more than 17 weeks (i.e. 120 days) nearly ambient temperature was reached inside the heap, indicating the completion of the main process.

The reason for this positive result apparently was not the addition of sewage sludge (which has a C/N-ratio of 7.6 only) but the mixing with MBT-residues as bulking material, causing improved aeration of the heap in trial #4.

The reduction of mass and volume observed after 120 day of composting is shown in Table 3. The characterisation of output (compost and sieve residues >20 mm) is reported in Table 4.

The results of Trials # 1÷# 4 are clearly indicating, that due to the extremely low C:N-ratio of wet white shavings (i.e. C/N = 3.2) successful results are only achieved, when enough carbon-rich amendment material is added for composting. If not, the duration of the composting process is getting too long (more than 17 weeks) and severe odor problems are appearing. After a process time of 120 days, the output materials of Trials #1÷4 were weighted for determination of the rotting-loss and afterwards screened with mesh-size 20 mm. The sieve underflow contains the raw compost, the sieve overflow the residue. Both of the fractions have been investigated and analysed at the laboratory of the Institute for Waste Management & Landfill Technology at Montan University, Leoben. The results obtained are shown in Table 3 and Table 4.

Table 3. Reduction of mass and volume (rotting loss) during compostation
Tabela 3. Redukcja masy oraz objętości (straty przez rozkład) w trakcie kompostowania

Trial	Rotting-Loss	
	Reduction of mass [%]	Reduction of volume [%]
#1: addition of straw	46	55
#2: addition of stable bed straw	42	51
#3: addition of biowaste	45	41
#4: addition of sewage sludge & MBT-residues	28	46

Table 4. Chemical and physical characterisation of output materials
Tabela 4. Chemiczna i fizyczna charakterystyka materiału wyjściowego

Parameter	**Unit**(*)	**Trial #1** **Straw**		**Trial #2** **Stable Bed Straw**		**Trial #3** **Biowaste**		**Trial #4** **Sludge & MBT-Residues**	
		Compost	Sieve Residue	**Compost**	**Sieve Residue**	**Compost**	**Sieve Residue**	**Compost**	**Sieve Residue**
pH	-	6.79	6.86	7.07	7.21	7.38	7.36	8.05	8.09
eL	mS/m	13.34	16.04	15.16	14.69	7.37	5.66	7.60	7.41
ADR	mg/kg	177,000	496,100	392,600	379,050	151,800	79,000	161,980	123,100
Pb	mg/kg	6.85	<5	6.19	6.78	25.35	24.72	42.11	30.54
Cd	mg/kg	<0.5	<0.5	<0.5	<0.5	0.64	0.67	0.72	0.67
Cr	mg/kg	82.2	82.6	434.9	341.7	258.8	288	300.6	463.2
Cu	mg/kg	16.74	9.50	30.45	28.95	65.79	58.77	177.7	150.9
Hg	mg/kg	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Zn	mg/kg	<125	<125	<125	<125	202.4	155.5	373.3	306
TOC	mg/kg (%)	272,301 (27.2%)	284,227 (28.4%)	293,236 (29.3%)	264,824 (26.5%)	230,238 (23.0%)	276,659 (27.7%)	193,073 (19.3%)	210.570 (21.0%)
WG	%	32.68	36.02	39.81	42.81	30.83	34.05	34.84	37.68
GV	%	91.42	92.68	85.08	85.24	61.40	68.08	53.12	55.14
K	mg/kg	4,927	4,192	13,290	12,260	11,805	10,050	11,557	10,097
Cl	mg/kg	9,329	10,421	11,074	11,254	6,765	8,289	8,078	8,695
S	mg/kg	0.89	0.89	1.04	0.91	0.66	0.63	0.54	0.57
C	%	42.1	42.4	39.6	39.7	30.0	33.7	26.0	27.5
N	%	8.8	9.2	6.7	7.0	3.8	3.5	3.4	2.9
H	%	5.4	5.6	5.0	5.0	3.7	4.2	3.0	3.2
P	mg/kg	732	633	1,944	2,403	3,798	4,500	6,443	4,355

(*) *Based on dry material*

It is obvious that the resulting C:N–ratio of the raw compost from all of the Trials (#1÷#4), is very low (range: 4.8 for Trial #1 – 7.9 for Trial # 3), compared to the C:N-ratio of compost given in literature (C/N=15÷20). To evaluate the fertiliser properties of the compost achieved in the reported Trials #1÷#4, plant tollerance tests were performed, using cress as the indicator plant. Not surprisingly, no plant growth but phytotoxicity could be observed for the fresh raw compost of all trials, due to the low C:N-ratio and high salt concentration (e.g.: chloride: between 0.6÷1.1% d.m.). Also the TOC-values of the raw compost (between 19%÷29%) were comparatively high, showing that the biological degradation of the substrate was not complete. Only after six month of maturation, modest cress growth was observed for the pot-tests performed.

3. Thermal treatment of wet-blue residues

3.1. Materials and Methods

When waste is used as additive in brick making, some practical requirements have to be met, like:

- no increase of emissions (and odors) during brick burning process,
- no uncontrolled formation of chromate (CrO_4^{2-}) or leaching of Cr_{VI} out of the product,
- no deterioration of product quality (i.e. mechanical & physical properties),
- no change in (red) brick color.

Hence, the following questions have to be answered in this work:

- Quantities (percentage) of wet blue shavings that can be mixed with clay matrix for brick making?
- Optimum brick burning temperature?
- Impact of waste addition on mechanical, physical and chemical properties of brick?
- Can the limit values (for Cr_{VI}) of the Standard Leaching Test be met, when used bricks are disposed of in a landfill for demolition waste?
- Can the immobilisation of chromium in the brick be improved by addition of auxiliary substances?

For answering these questions, a systematic as well as comprehensive lab-scale investigation has been carried out at Montan University Leoben. For the laboratory scale tests reported below, the following materials have been used, see Table 5 and Table 6.

Table 5. Characterisation of clay, used for the manufacturing of test bricks
Tabela 5. Charakterystyka gliny użytej do produkcji cegieł

Parameter	**Dry matter**	**LOI (at 1,050°C)**	**SiO_2**	**CaO**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**
Content [$\%_{dm}$]	81.82	7.71	65.90	1.12	1.08	14.63	5.43	0.57
Parameter		**K_2O**	**MnO**	**TiO_2**	**S**	**CI**	**P_2O_5**	
Content [$\%_{dm}$]		1.81	0.09	0.90	0.05	<0.02	0.16	

Table 6. Characterisation of wet blue shavings, used as additive for test bricks
Tabela 6. Charakterystyka wilgotnych błękitnych ścinek użytych jako dodatek do cegieł

Parameter	**UHV [kJ/kg]**	**LOI (at 1,050°C)**	**TOC**	**S**
Content [$\%_{dm}$]	14,335	87.93	30.35	2.91
Parameter	**P**	**Cr**	**Ca**	**Al**
Content [$\%_{dm}$]	0.0056	**3.89**	0.47	1.04
Parameter	**Fe**	**Mg**	**Na**	
Content [$\%_{dm}$]	0.052	0.0067	2.93	

UHV: Upper Heat Value, LOI: Loss of Ignition, TOC: Total Organic Carbon, d.m.: dry material, w.w.: wet weight

Test bricks were made by mixing about 50g of clay with different portions ($0\%_{w.w.}$, $1\%_{w.w.}$, $2.5\%_{w.w.}$, $5\%_{w.w.}$ and $7.5\%_{w.w.}$) of wet blue shavings specified in Table 6. The disk and plate ("biscuit") – shaped test bricks were air dried and finally burnt at well defined temperatures (i.e.T = 850, 950, 1,050 and 1,100°C respectively), using a lab-scale pottery oven.

When the possible influence of additives or auxiliary substances on the leaching behaviour of the test bricks has been investigated, another set of test-specimens were prepared, containing various portions of borax ($Na_2\,B_4\,O_7 \cdot 10\,H_2O$), silicafume ($S_iO_2$) and ferro-sulfate ($FeSO_4$) as immobilisation – additive for chromium. The mass of a test brick was ca. 50 g in raw state and became ca. 40 g and ca. 35 g after air drying and burning respectively.

The following investigations, tests and analyses have been carried out:

- Physical and mechanical properties:
  - Raw Density [g/cm^3]
  - Water uptake capacity [%TS]
  - Longitudinal change (Shrinkage) [%]
- Chemical properties & leaching behaviour:
  - Chemical analyses (by XRF, AAS and IC)
  - Standard Leaching Test (24 hours, deionised H_2O; S:L-ratio = 1:10)
- X-Ray Diffraction Analysis (XRD)
- Differential – Thermogravimetric Analysis (TG und DTG)

3.2. Experimental results

3.2.1. Raw density of bricks

The relationship between the raw density [g/cm^3] of the test bricks and the amount (portions) of wet blue shavings added for brickmaking is show in Figure 3 for test specimes burnt at various temperatures.

Raw density and porosity are inverse quantities. As expected, with increasing portions of wet blue shavings added and/or decreasing brick burning temperatures the raw density of the test specimens becomes less because of increasing porosity.

3.2.2. Water uptake capacity of bricks

The influence of (a) amount of wet blue shavings added, (b) exposure time (soaking period) and (c) brick burning temperature on the test specimen has been investigated and the corresponding results are shown in Figure 3 to Figure 5.

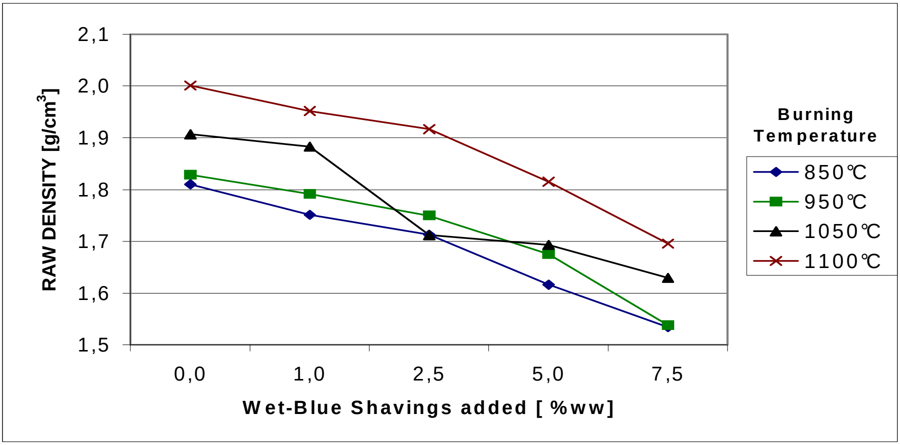

Fig. 3. Raw density of test bricks burnt at various temperatures plotted vs. amount (portions) of wet blue shavings added to clay for brickmaking

Rys. 3. Masa właściwa cegieł wypalonych w różnych temperaturach w zależności od ilości (porcji) wilgotnych niebieskich ścinek dodanych do gliny w procesie wytwarzania cegieł

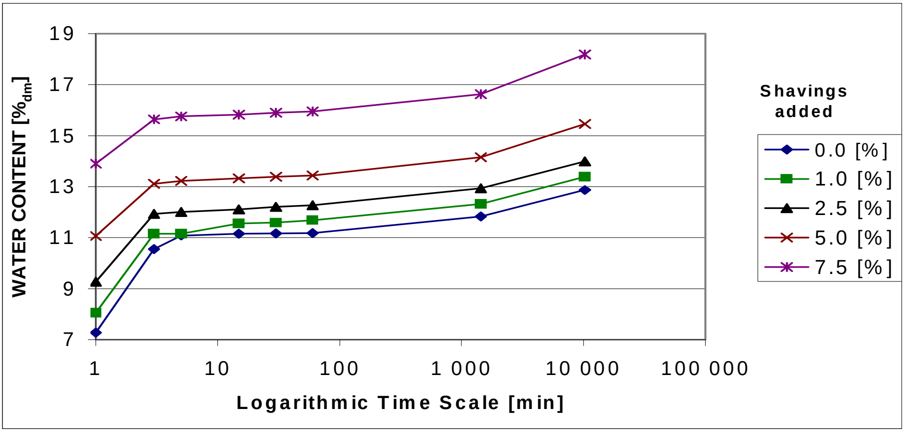

Fig. 4. Water up-take of various test bricks burnt at 950°C, plotted vs. soaking time
Rys. 4. Nasiąkliwość różnych cegieł wypalonych w temperaturze 950°C w zależności od czasu moczenia

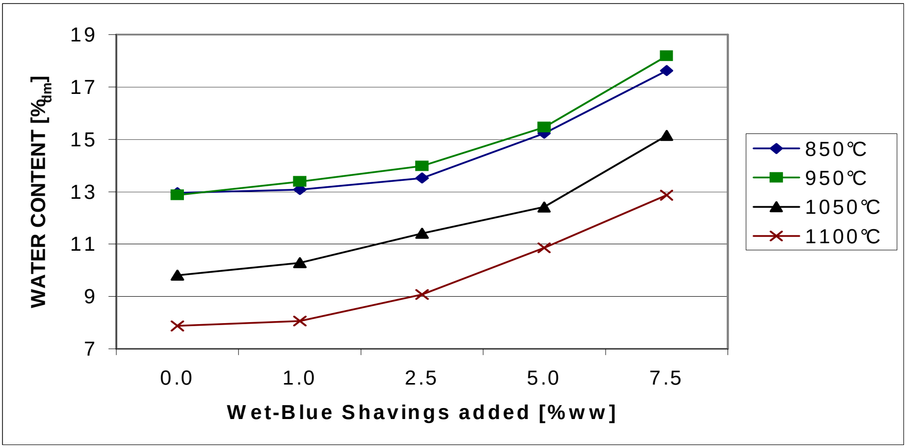

Fig. 5. Water up-take of test bricks burnt at different temperatures after 210 hours of soaking as function of the amounts (portions) of wet blue shavings added
Rys. 5. Nasiąkliwość cegieł wypalonych w różnych temperaturach po 210 godzinach moczenia w funkcji ilości (porcji) dodanych wilgotnych niebieskich ścinek

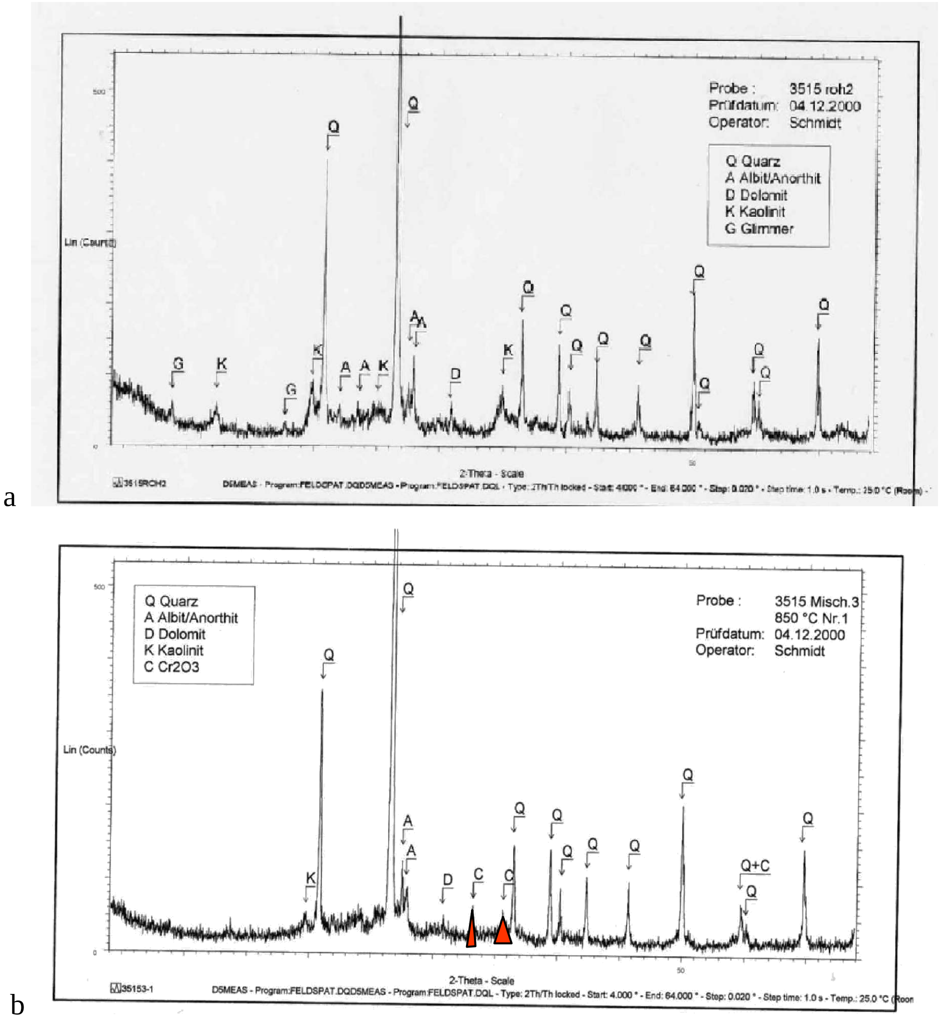

Fig. 6. XRD-spectrum of test brick, made without addition of wet blue shavings (a) and by addition of 5%$_{ww}$ wet blue shavings (b) at burning temperature of 1050°C
Rys. 6. Spektrum XRD cegły zrobionej bez dodatków (a) i z dodatkiem 5%$_{mm}$ wilgotnych niebieskich ścinek (b) przy temperaturze wypalania 1050°C

As shown above, the water up-take [%$_{d.m.}$] of the test specimens increases with the soaking period and the amount (portion) of wet blue shavings added to the clay. These results prove the formation of pores inside the bricks with increasing amounts of wet blue shavings added.

Obviously, the water uptake of the test bricks increases with increasing amounts of wet blue shavings added and with decreasing brick burning temperature. At 1,100°C, the formation of pores inside the bricks is much less, compared to a burning temperature of 850÷950°. Altogether, the observed water uptake capacity of the investigated test brick was in the acceptable range for normal bricks, and the results are corresponding with the raw density of the test bricks in 3.1.

3.2.3. X-Ray Diffraction (XRD)-Analysis

By XRD-analysis, the mineral phases of the samples can be identified. One could expect changes in the XRD-spectrum of test specimens containing wet blue shavings compared to normal bricks (blanks).

When comparing the spectra, the formation of Cr_2O_3 mineral phase can be observed in test bricks made by addition of wet blue shavings which contain $CrSO_4$. It was found that the Cr_2O_3-peak increases with increasing burning temperatures of the specimens.

3.2.4. Thermogravimetric (TG&DTG) analysis

Using Thermogravimetric (TG) and Differential Thermogravimetric (DTG) analysis, exothermal and endothermal reactions as well as increase or decrease of mass at various temperatures can be observed for the sample to be tested.

Once again one could expect differences in the TG and DTG-curves of specimens having different compositions. A comparison between the 3 obtained curves reveals these differences. Up to a temperature of about 400°C, there is no significant difference for clay samples with and without wet blue shavings added. Fig. 7b shows a strong exothermal reaction (with 2 peaks at 458 and 507°C) and a weight – loss of 5.5% between 400÷560°C, due to the oxidation of organic matter and cleavage of CO_2 in the test sample made by addition of wet blue shavings. When $5\%_{ww}$ $FeSO_4$ is added to the clay for immobilisation of chromium (see Fig. 7c) the strong exothermal oxidation of the wet blue shavings is shifted to higher temperatures (i.e. 488 and 551°C respectively). At about 600°C another weight loss can be observed from the TG-curve, probably due to the cleavage of SO_3 from ferrosulfate added. When $1\%_{ww}$ borax and $4\%_{ww}$ silicafume were added to the clay for brick making together with $7.5\%_{ww}$ wet blue shavings, the resulting TG and DTG-curves became similar to the one shown in Fig. 7b, except for the two exothermal oxidation peaks which were shifted to 466°C and 520°C respectively.

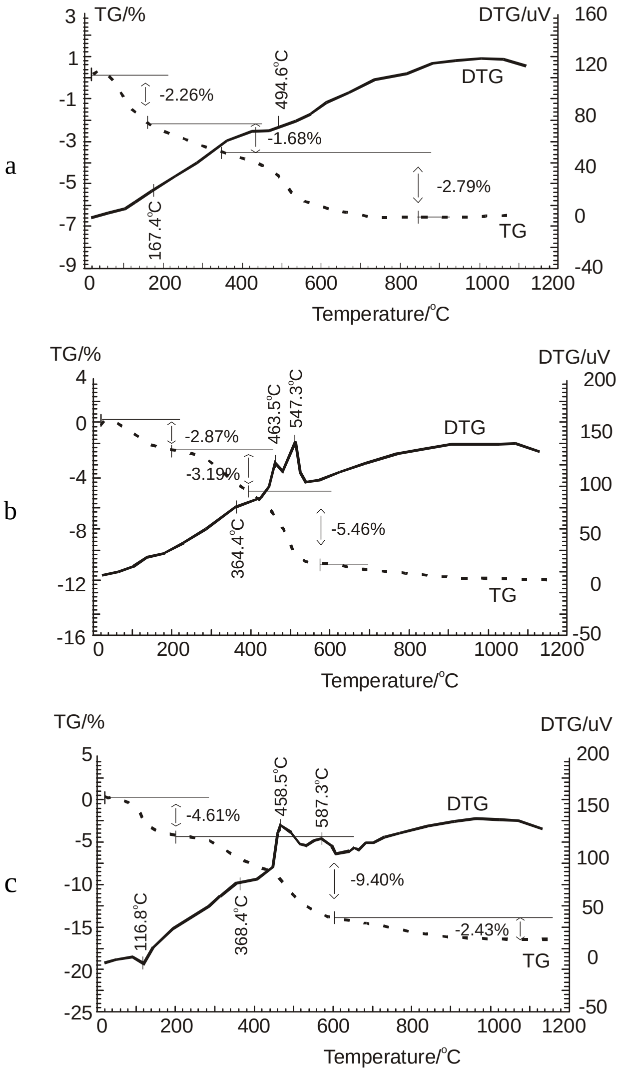

Fig. 7. TG and DTG curves for the different test bricks: a – for air dried test-bricks made without wet blue shavings (blank); b – air dried test bricks made with 7.5%$_{ww}$ wet blue shavings added; c – air dried test bricks made with 7.5%$_{ww}$ wet blue shavings and 5%$_{ww}$ $FeSO_4$ added

Rys. 7. Krzywe TG i DTG różnych cegieł: a – suszonych na powietrzu, wyprodukowanych bez dodatków (zerówka); b – suszonych na powietrzu, wyprodukowanych z dodatkiem 7,5%$_{mm}$ wilgotnych niebieskich ścinek; c – suszonych na powietrzu, wyprodukowanych z dodatkiem 7,5%$_{mm}$ wilgotnych niebieskich ścinek i 5%$_{mm}$ $FeSO_4$

3.2.5. Standard Leaching Test

A main criterion whether wet blue shavings can be used for brickmaking or not is the leaching behaviour of chromium incorporated in the bricks. During brick burning, oxidation of Cr^{3+} to CrO_4^- (chromate) cannot be excluded, especially under alkaline conditions. Alkali chromate is highly soluble and toxic as well. Hence, leaching of Cr_{VI} may cause severe environmental problems, when used bricks and rubble are disposed of in demolition waste landfills. Thus, bricks made by addition of wet blue shavings in any case must meet the limit value for chromium (Cr_{total}) or chromate (Cr_{VI}) laid down in the regulations for the leachate of landfills. In Austria, for a type II landfill (for demolition waste), the following limit values are compulsory:

Limit concentration in leachate: 0.05 mg/L for Cr_{VI} and 0.2 mg/L for Cr_{total}. Total content of chromium in solid waste sample: not more than 500 mg/kg_{dm} for Cr_{total}.

The standard Leaching Test (i.e. 24 hours shaking of crushed sample with deionized water, at solid: liquid ratio 1:10) is used for testing the waste samples for compliance with the regulation of the Landfill Ordinance.

In Figure 8, Standard Leaching Test-results are shown for various test bricks, made with different portions of wet blue shavings added and burnt at different temperatures.

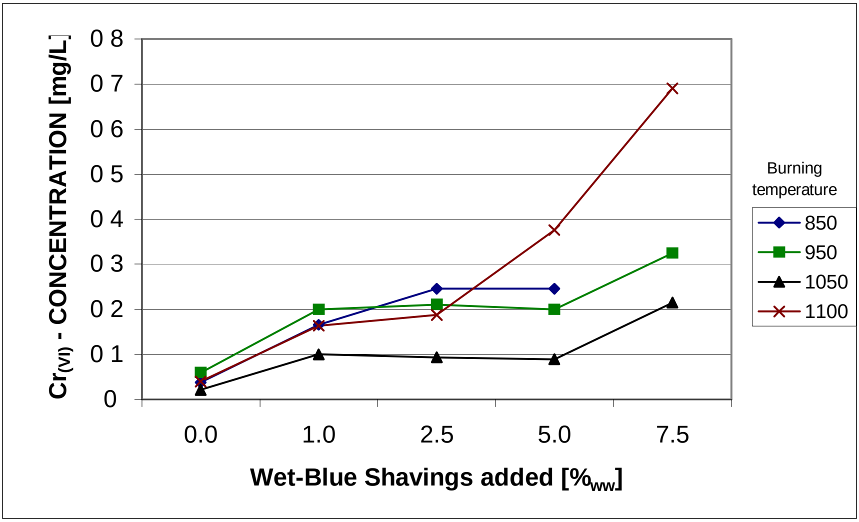

Fig. 8. $Cr_{(VI)}$-leachate concentration of test bricks burnt at various temperatures plotted vs. amount (portions) of wet blue shavings added for brickmaking

Rys. 8. Stężenie Cr(VI) w odcieku z cegieł wypalonych w różnych temperaturach w zależności od ilości (porcji) dodanych wilgotnych niebieskich ścinek

The pH-values measured in the leachate were pH 9.7÷9.9 for bricks made without wet blue shavings and pH 8.5÷9.9 for bricks made with wet blue shavings.

Minimum leaching of chromium ($Cr_{VI} = Cr_{total}$) seems to be reached by a brick burning temperature of 1,050°C. As shown in Figure 8 the average Cr_{VI}-concentration in the leachate was about 0.2 mg/L, corresponding to a portion of soluble chromium in the bricks which is less than 0.05÷0.1% of the total chromium incorporated. Nevertheless, none of the test specimens could meet the stringent national limit value of 0.05 mg/L Cr_{VI} for demolition waste landfills.

3.2.6. Immobilisation of chromium in bricks

For developing countries where environmental regulations are not as strict as in Austria, 0.2 mg/L Cr_{VI} in leachate may be tolerable for bricks. However it was the intention of the authors to develop a procedure for the immobilisation of chromium in bricks made with wet blue shavings, so that tannery wastes can be used for brickmaking in Europe too. For that reason, trials have been carried out for the enhanced immobilisation of chromium in bricks by addition of auxiliary substances. The additives tested were borax ($Na_2B_4O_7 \cdot 10\ H_2O$) with silicafume ($SiO_2$) (see Figure 9) and ferrosulfate ($FeSO_4$) (see Figure 10).

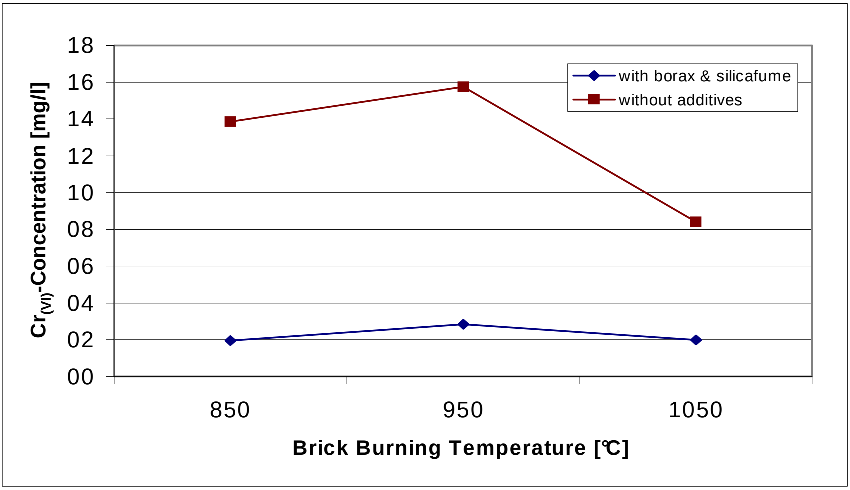

Fig. 9. $Cr_{(VI)}$ concentrations in leachate for test bricks with & without borax & silicafume, burnt at various temperatures

Rys. 9. Stężenia Cr(VI) w odcieku z cegieł z dodatkiem boraksu i krzemionki wypalonych w różnych temperaturach

For fixation of chromium in the solid phases of the bricks, the following mixture was prepared for brickmaking (Figure 9): 87,5%$_{ww.}$ clay, 7.5%$_{ww.}$ buffing dust (instead of wet blue shavings), 4%$_{ww.}$ $Na_2B_4O_7 \cdot 10\ H_2O$ (borax) and 1%$_{ww.}$ SiO_2 (silicafume). When Figure 9 is compared with Figure 8, it becomes obvious that the Cr_{VI} leaching is more for bricks prepared with buffing dust compared to bricks made with addition of wet blue shaving. For that reason, the following trails for immobilisation of chromium in bricks were made with specimens containing buffing dust instead of wet blue shavings.

In the next trial, the mixture was tested (Figure 10): 87.5%$_{ww}$ clay, 7.5%$_{ww}$ buffing dust and 5%$_{ww}$ $FeSO_4$. The test specimen without additives were made with 92.5%$_{ww}$ clay and 7.5%$_{ww}$ buffing dust only.

As a result, the addition of both additives can significantly reduce the leaching of Cr_{VI} from the bricks. There seems to be an influence of the brickburning temperature too, with minimum leaching at 1,050°C. In Figure 11, the measured pH-values of the leachate is plotted vs. the brickburning temperature of the investigated specimens.

Apparently at higher brick burning temperatures, the pH becomes alkaline and leaching of chromium becomes less.

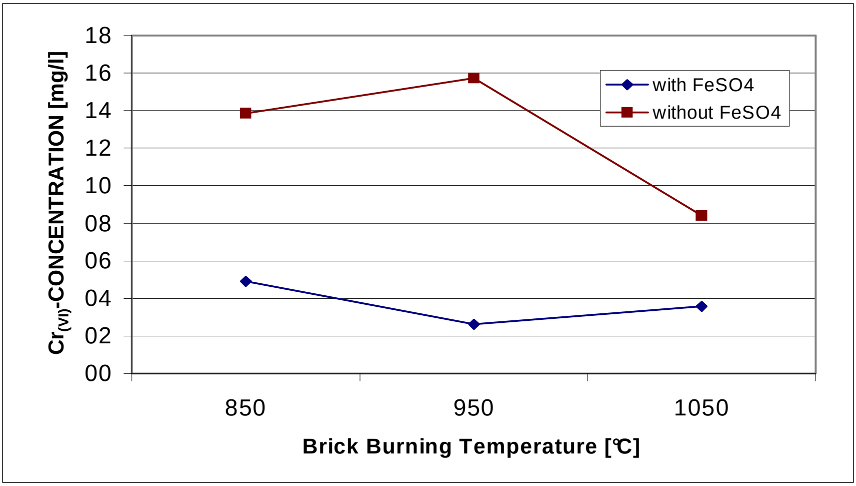

Fig. 10. $Cr_{(VI)}$ concentrations in leachate for test bricks with & without ferrosulfate, burnt at various temperatures

Rys. 10. Stężenia Cr(VI) w odcieku z cegieł wypalonych w różnych temperaturach z dodatkiem $FeSO_4$ i bez

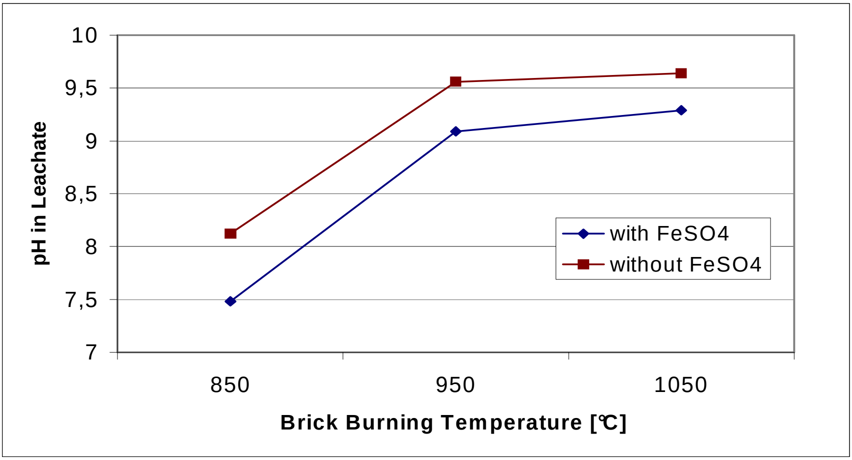

Fig. 11. pH-values of leachate from various specimens, made with and without $FeSO_4$ – addition and burnt at different temperatures

Rys. 11. Wartości pH odcieków w różnych przypadkach, z dodatkiem i bez dodatku $FeSO_4$ i wypalonych w różnych temperaturach

4. Conclusions

4.1. Aerobic treatment of wet-white shavings

The following conclusions can be drawn for the practical application of open windrow composting of wet-white shavings to produce valuable compost, which can be used as fertiliser in agriculture:

- Monocompostation of wet white shavings (tannery waste) is not possible, because of the high nitrogen-content (i.e. 14.5% d.m.) and consequently low C:N-ratio (i.e. C/N = 3.2) of the waste material.
- The addition of carbon-rich, biodegradable amendment for composting is a must, for increasing the C:N-ratio to about C/N = 30.
- To achieve reasonable results, the portion of wet white shavings in the mixture for composting should not exceed 5÷10% d.m., with 30÷40% d.m. bulking material and 50÷60% of carbon-rich, biodegradable amendments.
- Hence, co-compostation of wet white shavings together with biowaste (from separate household waste collection) is recommended, which could be done at (MBT)-plant or at the tannery site, if enough amounts of amendments are available.
- The compost produced by co-compostation of wet white shavings is low on heavy metals (see Table 4), and when matured, it can be used as a fertiliser in agriculture.

- Compostation of wet white shavings to produce fertiliser seems to be a good approach for waste management in tanneries, as the so far practised disposal by landfilling will not be allowed anymore in most of European Countries because of environmental impacts. It also seems to be advantageous for developing countries, because it offers a reasonable way for waste utilisation in tanneries and for supplying local farmers with low cost compost-fertiliser.

4.2. Thermal treatment of wet-blue residues

Up to 7.5% wet blue shavings as well as buffing dust were mixed with clay for making test bricks, which were burnt at 850, 950, 1,050 and 1,100 °C respectively. In laboratory test series, the physical, mechanical and chemical properties of the test specimens have been investigated. The results obtained or the determination of raw density, water uptake capacity, longitudinal shrinkage and color showed no negative effect on brick quality by addition of wet blue shavings and buffing dust (portions added: $1 \div 7.5\%_{w.w.}$).

- The crucial parameter for the utilisation of tannery wastes in brick industry is leaching of chromate (Cr_{VI}), which was determined by the Standard Leaching Test. Leaching of Cr_{VI} was found to take place in the 0.05÷0.1% range of total chromium incorporated in the bricks. This may be satisfactory for developing countries, but it cannot meet the stringent Austrian limit values for disposal of used bricks and rubble in a demolition waste landfill-type.
- For improving the immobilisation of chromium, borax and silicafume as well as ferrosulfate were added to brickmaking. The results achieved are positive, as both additives significantly reduced the leaching of Cr_{VI}. Ferrosulfate ($FeSO_4$), which is an industrial waste, should be easily available on the market and hence could be used as inexpensive additive for improving the leaching behaviour of chromium, when wet blue shavings or buffing dust are used for brickmaking.
- For immobilisation of chromium as Cr_2O_3 inside the bricks, a burning temperature of about 1,050 °C seems to be favourable too. For practical applications, about $1\%_{ww}$ of wet blue shavings should be added to the clay, which corresponds to about 450 $mg/kg_{ww.}$ chromium in brick.

So far, the laboratory scale tests for utilisation of chromium containing tannery wastes in brick industry are positive and the results achieved are promising, but large scale pilot plant trials with real size test bricks are necessary, before a final statement can be given whether this product made by addition of waste has a real chance on the market or not.

Gospodarka i utylizacja odpadów pochodzących z przemysłu garbarskiego

Streszczenie

W czasie procesu golenia skór (gdy doprowadzane są one do jednolitej grubości) powstają odpady: **białe wilgotne ścinki** (gdy w czasie procesu używany jest glutar-dialdehyd) lub **niebieskie wilgotne ścinki** (gdy w czasie procesu stosowany jest chrom).

W pracy przedstawiono badania utylizacji tych odpadów. Do utylizacji białych wilgotnych ścinek zastosowano proces tlenowego kompostowania, ponieważ jest to metoda prostsza i tańsza w porównaniu z beztlenowym przetwarzaniem w komorach w celu uzyskania biogazu. A więc powinna ona być odpowiedniejsza dla krajów rozwijających się. Do drugiego rodzaju odpadów zastosowano metodę termiczną – użycie wilgotnych niebieski ścinek jako dodatku do produkcji cegieł. Głównym celem tej metody jest immobilizacja chromu.

Na podstawie wyników w pierwszej części badań można stwierdzić:

- Aby uzyskać sensowne wyniki porcja dodawanych wilgotnych białych ścinek do kompostowania nie powinna przekraczać 5÷10% sm, dodatek materiału strukturotwórczego powinien wynosić 30÷40% sm a bogatych w węgiel, biodegradowalnych dodatków 50÷60% w celu podniesienia stosunku C:N do wartości ok. 30.
- Zalecane jest kompostowanie wilgotnych białych ścinek wraz z bioodpadami (z selektywnej zbiórki odpadów).
- Kompost wyprodukowany z wilgotnych białych ścinek zawiera znikome ilości metali ciężkich (tabela 4), i dojrzały może być stosowany jako nawóz w rolnictwie.

Wyniki uzyskane w drugiej części badań dotyczących termicznej utylizacji niebieskich wilgotnych ścinek pokazują:

- Dodatek niebieskich wilgotnych ścinek i odpadowego pyłu z polerowania skór w ilości 1÷7.5% mm (mokrej masy) do wypalanych cegieł nie spowodował żadnego negatywnego wpływu na jakość wyprodukowanych cegieł.
- Z cegieł wymywało się 0.05÷0.1% całkowitej zawartości chromu w cegłach. Wynik ten jest satysfakcjonujący dla krajów rozwijających się. Natomiast w Austrii nie spełnia on ostrych norm dotyczących składowania zużytych cegieł i odpadów budowlanych.
- Aby polepszyć immobilizację chromu dodawano w procesie produkcji cegieł boraks i krzemionkę oraz $FeSO_4$. Oba dodatki znacząco redukują wymywanie chromu. Siarczan żelazawy, który jest odpadem przemysłowym, powinien być łatwo dostępny na rynku i tani.
- Temperatura wypalania wynosząca ok. 1050°C wydaje się być najkorzystniejsze w celu ograniczenia wymywalności Cr (VI).