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A Method of Utilization of Polyurethane after the End of Its Life Cycle

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1. Introduction

The utilization of secondary raw materials represents a very important segment in terms of environmental protection and when ensuring permanently sustainable development. Its goal is a permanent research of the hidden utilization potential of produced waste materials. The issue of the utilization of waste materials from coal mining by means of innovative technologies is described in [1], the utilization of mineral waste in the construction of municipal waste landfills is described in [2], and the possible application of waste sands in the industrial floors segment is described in [3].

Landfilling is still the most widespread method of waste disposal in the Czech Republic. This is mainly due to high charges for depositing waste in landfills and poorly developed infrastructure and capacity of other technical facilities for waste treatment. It is necessary to add that CR has very favourable geological conditions for construction of landfills.

The second most common way of dealing especially with construction waste materials in the Czech Republic is their recycling and subsequent reuse. The following recycled material resources are currently used in building practice: concrete, bricks, tiles, ceramics, asphalt mixtures without hazardous properties, soil and aggregates without hazardous mixtures. In Table 1, we present an overview of production of construction waste in the Czech Republic during the period from 2006 to 2010, serving as an input for the recycling process itself. The data are taken from the ISOH database, administered by the Czech Environmental Information Agency (CENIA). However, these values (with regard to the current definition of waste in the Waste Law 185/2001 of the Code) do not affect the production of all subjects, but especially the weight aspect of the key types of inert mineral construction waste from groups 1701, 1703 and 1705. According to the definition: "Waste is any movable asset its owner disposes of or intends or is bound to dispose of and it belongs to some of the groups of wastes listed in Annex no.1 to this Law." (Law 185/2001 of the Code § 3, paragraph 1). Nevertheless, a significant part of the excavated soil and aggregate and other inert construction wastes do not comply with this definition if, after recycling (usually at the demolition site), they do not change their owner (the recycling company acts only as a form of service here). That is why the inert mineral wastes recycled this way or products derived from them usually do not go through the above-mentioned ISOH database [4].

According to Annex No. 1, the Ministry of Environment Decree No. 381/2001 of the Code, polyurethane foam after the end of its life cycle, used as a waste material for recycling, can be assigned code 07 02 13, according to the catalogue of waste materials. The Czech Republic has an annual production of about 40 000 tons of waste fitting the above mentioned code, and about 10 000 tons of this waste is rigid polyurethane foam.

Current methods of rigid polyurethane foams recycling which are used in the world are described in Fig. 1. The best way to recycle polyurethane foam at the end of its life cycle, as filler in restoration mortars, is its disintegration in a knife mill. Polyurethane foam recycled by means of this method is suitable as a substitute of expanded volcanic glass – pearlite, expanded obsidian and expanded vermiculite. Other ways of recycling polyurethanes into feedstock or as decomposition into individual components of monomers [5, 6] using a chemical method, together with burning and subsequent energy recuperation [7, 8], may appear to be some of the best practices of recycling plastics, but none of these methods of recycling provides suitable filler for restoration mortars.

Table 1. Production of construction and demolition wastes in the Czech Republic in the period of 2007–2010

Tabela 1. Produkcja budowlanych i rozbiórkowych odpadów w Czechach w latach 2007–2010

Group	Waste	Year 2007 [kt]	Year 2008 [kt]	Year 2009 [kt]	Year 2010 [kt]
17 01	**Concrete, bricks, tiles and ceramics**	**4 628**	**2 934**	**2 998**	**3 167**
17 01 01	Concrete	1 815	1 224	1 132	1 163
17 01 02	Bricks	761	861	919	834
17 01 03	Tiles and ceramic products	12	13	15	18
17 01 06*	Mixtures containing dangerous substance	82	43	46	22
17 01 07	Mixtures not listed under No. 17 01 06	1 958	793	886	1 130
17 03	**Asphalt mixtures, tar and tar products**	**505**	**445**	**516**	**466**
17 03 01*	Asphalt mixtures containing tar	11	8	3	10
17 03 02	Asphalt mixtures not listed under No. 17 03 01	493	437	513	456
17 03 03*	Coal-tar and tar products	1	0	1	0
17 05	**Soil (including soil extracted from contaminated places), aggregate and extracted tailings**	**9 176**	**11 396**	**10 707**	**10 846**
17 05 03*	Soil and aggregate containing dangerous substance	314	462	504	280
17 05 04	Soil and aggregate containing dangerous substance, not listed under No. 17 05 03	8 481	10 026	9 116	8 825
17 05 05*	Extracted tailings containing dangerous substances	0	0	0	0
17 05 06	Extracted tailings not listed under No. 17 05 05	292	707	1 003	1 687
17 05 07*	Ballast from superstructure containing NL	10	26	30	7
17 05 08	Ballast from superstructure not listed under No. 17 05 07	79	175	54	47
17 09	**Other construction and demolition wastes**	**702**	**497**	**580**	**622**
17 09 03*	Other construction and demolition wastes containing dangerous substances	59	47	95	67
17 09 04	Mixed construction and demolition wastes not listed under Nos. 17 09 01, 17 09 02 and 17 09 03	642	449	485	555
Total		**15 065**	**15 272**	**14 802**	**15 101**

Source: ISOH database – Waste Management Information System (CENIA – Czech Environmental Information Agency)

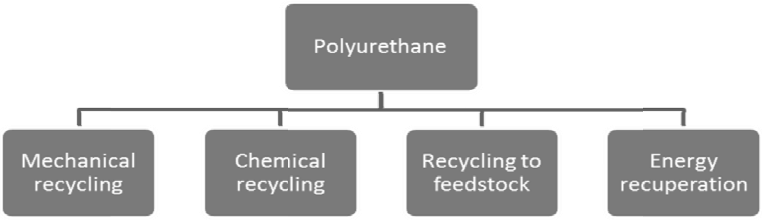

Fig. 1. Scheme of current recycling methods of rigid polyurethane foam
Rys. 1. Schemat obecnych metod recyklingu sztywnej pianki poliuretanowej

2. Materials

2.1. Recycled rigid polyurethane foam

3 samples of crushed rigid polyurethane foam were prepared for the purposes of experimental research. The crushing was performed using a knife mill and output screens with 6 and 8 mm in size. All samples were later subjected to grain analysis. The screen analyses were conducted on a laboratory sifting machine with standardized screens according to ČSN EN 933-1. The grain analysis was performed using selected series of screens: 0.063, 0.125, 0.25, 0.5, 1, 2, 4, 5.6, 8 mm. The outcomes of the grain analysis are presented in Table 2 and in Fig. 2.

Table 2. Sift analysis of VST01 – VST03 samples
Tabela 2. Analiza Sift próbek VST01 – VST03

Screen size [mm]	Siftings percentage summary [%]		
	VST01	VST02	VST03
0.063	12.80	12.50	12.30
0.125	12.90	12.50	12.60
0.25	13.40	12.70	13.00
0.5	15.40	13.50	14.60
1	26.30	22.30	24.70
2	54.50	52.80	55.60
4	94.50	97.30	96.20
5.6	98.80	99.90	98.30
8	100.00	100.00	100.00

Polyurethanes in fact respect the size of the screen installed in the knife grinder. However, the maximum size of crushed material has an initial measurable volume one or two orders bellow the size of the screen installed in the crusher.

The graphic presentation of the grain size curves (see Figure 2) clearly shows that the siftings of grain size of 2 mm for all polyurethane samples is 55% of the sample weight. Crushed polyurethane foam samples show an even share of particles of 2 – 4 mm grain size range.

Samples of crushed polyurethane foam VST01, VST02, VST03 were subjected to aqueous leach tests according to Government Regulation No. 163/2002 of the Code. The purpose was to determine whether the samples are not contaminated with excess concentrations of heavy metals and volatile organic compounds. The results of the analyses are presented in Tables 3 and 4. The acceptable values according to this Regulation are marked LIMIT in the table.

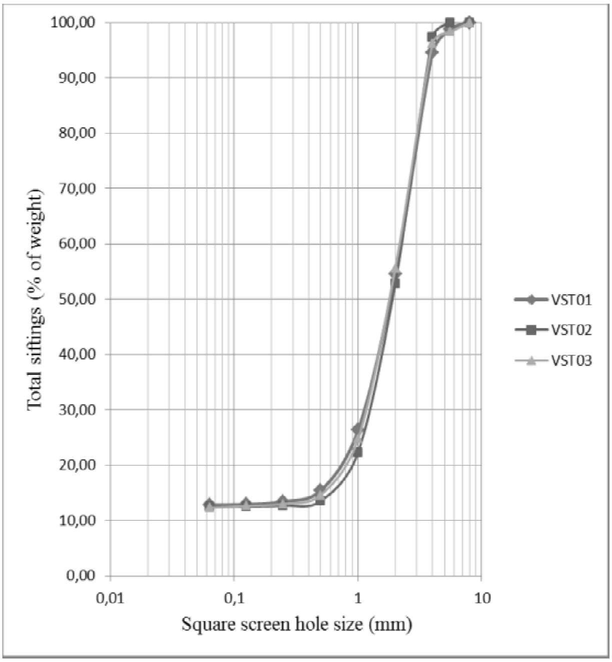

Fig. 2. Graphic expression of grain size curve of VST01 – VST03 samples
Rys. 2. Graficzna ilustracja krzywej granulometrycznej próbek VST01 – VST03

Table 3. Results of contamination analyses of recycled polyurethane foam samples
Tabela 3. Wyniki analiz zanieczyszczeń próbek pochodzących z recyklingu pianki poliuretanowej

Anal. Subst.	TOC	COD	Mn	pH	Cr	Pb	Cd	Ni
	[mg · l^{-1}]				[mg · l^{-1}]			
VST01	0.163±0.028	<6	<0.03	6.01±0.13	<0.03	<0.02	<0.002	<0.03
VST02	0.447±0.076	<6	<0.03	6.30±0.13	<0.03	<0.02	<0.002	<0.03
VST03	0.419±0.072	<6	<0.03	6.82±0.14	<0.03	<0.02	<0.002	<0.03
LIMIT	5	(Mn)3.0	0.05	6.5–9.5	0.05	0.01	0.005	0.02

Table 4. Results of contamination analyses of recycled polyurethane foam samples
Tabela 4. Wyniki analiz zanieczyszczeń próbek pochodzących z recyklingu pianki poliuretanowej

Anal. Subst.	Phenols	Formalde-hyde	Benzene	Toluene	Σ xylene	o-xylen+ styren	Ethylbenze-ne	TCE	PCE
	[mg · l^{-1}]								
VST01	<0.05	0.00006	<0.001	0.001	<0.001	0.022	<0.001	<0.001	<0.001
VST02	<0.05	0.00007	<0.001	0.003	<0.001	0.029	<0.001	<0.001	<0.001
VST03	<0.05	0.00006	<0.001	<0.001	0.001	0.029	<0.001	<0.001	<0.001
LIMIT	0.05	–	0.001	0.2	0.2	*0.02	0.02	0.01	0.01

*only styrene

The results of the analyzes of the polyurethane foam samples presented in Tables 3 and 4 clearly show that the limit value has not been exceeded in any of the monitored parameters.

2.2. Bonding agents and additives

Mixed Portland cement CEM II 32,5N-S was used as the main bonding agent in mixtures for restoration mortars. Very finely ground limestone (Kotouč Štramberk), hydrate CL 90-S (Kotouč Štramberk) were used as well. The used additives were based on sodium alkylbenzene sulphonate, calcium lignosulphonate, copolymer vinylacetate and zinc stearate in order to improve the workability, rheology, content of air pores and hydrophobization.

3. Experimental part

3.1. Restoration mortar

6 recipes with different ratio of polyurethane bonding agents and additives were prepared for restoration mortar. The objective of the proposal was to discover a suitable ratio of components and suitable admixtures for modification of restoration mortars with polyurethane filler. Crushed polyurethane foam with grain size of 0–2 mm was used as the filling agent. It was acquired through sieving from sample VST02. Cement CEM II 32,5 N, hydrate, and very finely ground limestone were used in various ratios as the basic bonding agent. The recipes for restoration mortars are presented in Table 5.

Table 5. Recipes of restoration mortars
Tabela 5. Receptury zapraw renowacyjnych

Plaster mixture components	Unit	ZO1	ZO2	ZO3	ZO4	ZO5	ZO6
PUR (fr.0/2 mm)	g	4600	4600	4600	4600	4600	3100
Water	g	13000	13000	13000	14000	14000	11000
Cement CEM II 32.5N	g	12500	12500	12500	10500	10500	10500
Sodium alkylbenzene sulfonate	g	177	177	177	300	300	300
Calcium lignosulfonate	g	–	–	50	30	20	20
Copolymer vinylacetate	g	–	–	–	50	60	60
Hydrate CL90-S	g	–	2890	–	–	–	–
Very finely Grodnu limestone	g	5250	–	–	–	–	–
Zinc stearate	g	–	–	–	–	55	55

The individual mixtures were prepared in a horizontal mixer with forced circulation with the geometric volume of 80 dm^3. Exactly specified amount of polyurethane crumbs was measured for each mixture, and the individual components of bonding agents and additives were gradually added to the mixtures. The experimental mixtures prepared using this method were tested in order to determine the spreadable time and the time of fresh mortar treatment, and they were subsequently applied in the test forms. The forms were compacted for 10 seconds on a vibration table. The samples in forms were packed in polyethylene bags and stored in a room at temperature of 22 °C for 2 days, after that the forms were removed and the samples were put back in bags and stored for further 5 days. After this time, the frames were stored freely in the room at a temperature of 22 °C for 21 days. They were subsequently tested to determine the volume weight of dry hardened mortars, the strength of hardened mortars in compression, and the adhesive strength of hardened mortars for interior and exterior plasters. The test results are presented in Table 6.

Table 6. Test results of experimental mixtures of restoration mortars
Tabela 6. Wyniki badań eksperymentalnych mieszanek zapraw renowacyjnych

Marking	Strength of mortar in compression [$N \cdot mm^{-2}$]	Volume weight of hardened mortar [$kg \cdot m^{-3}$]	Spreadable time [min]	Backing adhesive strength [$N \cdot mm^{-2}$]	
				Value	Separation method
ZO1	0.44	550	60	0.040	in mortar
ZO2	0.47	500	60	0.040	in mortar
ZO3	0.35	430	60	0.030	in mortar
ZO4	1.00	350	60	0.050	in mortar
ZO5	1.20	350	60	0.051	in mortar
ZO6	1.20	300	60	0.053	in mortar

ZO 6 mixture, which had shown the best physical and mechanical properties of all the prepared formulae, was selected for further research. In this mixture, we have managed to reduce the value of volume weight of hardened mortar to 300 $kg \cdot m^{-3}$, while increasing its strength in compression to 1.2 $N \cdot mm^{-2}$ by adding a suitable ratio of lightening additives, additives increasing plasticity and altering the compressive strength. The backing adhesive strength has slightly increased to 0.053 $N \cdot mm^{-2}$, while maintaining the spreadable time of 60 minutes. The results of additional tests of mixture ZO6 are presented in Table 7.

Table 7. The results of additional tests of mixture ZO6
Tabela 7. Wyniki dodatkowych badań mieszanki ZO6

Restoration mortar mixture	Crushed polyurethane grain fineness [mm]	Bending strength in tension [MPa]	Mort. backing adhesive strength – Porobeton [MPa]	Water–vapour diffusion	C-value coefficient [$W \cdot m^{-1} \cdot K^{-1}$]	Capillary absorption coefficient [$kg \cdot m^{-2}$] after 24 h
ZO6	0.125–2	0.956	0.04	4.2	0.079	4.23

3.2. Application of restoration mortar

After removing the existing plasters and mechanical cleaning of the base wall, restoration mortar is applied in a thickness of 30–50 mm directly on the masonry. After rough levelling, there will be a highly porous structure that protects the masonry against negative effects (exposure of the exterior enclosure wall to freezing temperatures, thermal stress, rain water, the impacts of air and also to biological effects, i.e. algae, mosses, organic dust particles, efflorescence, etc.), however, thanks to its high internal surface and suitable pore size, it allows a trouble-free aeration of the masonry and it also prevents capillary action into the un-affected parts of the masonry. Eventual salt extracts are transferred to restoration mortar, so that they will not cause any further damage to the masonry. Even drying of the building is another positive factor, which is especially important for hybrid constructions □ clay, lime, unburned brick, stone, poro-concrete. Once the building has been dried, it is necessary to assess the condition of the restoration mortar and the base masonry and if it is not affected by the degradation effects, it is possible to leave it in the building as a core plaster for interior constructions, eventually as a thermal insulating plaster of the external siding of buildings.

4. Conclusion

Given the current amount of polyurethane waste and its expected increase in future years, the processing of polyurethane foam after the end of its life cycle as fillers for restoration mortars is currently very important. The benefits lie in a new method of the utilization of the recycled polyurethane foam after the end of its life cycle in the restoration mortars segment. It is based on the fact that the utilization of this recycled material as filler can represent a full-fledged substitution of the currently used light fillers based on expanded pearlite, obsidian, and vermiculite.

When comparing the characteristics of experimental mixture 6 presented in Tab. 6 and 7, in particular the thermal conductivity coefficient λ, with the properties of restoration mortars compared by us: weber – weber.san MONO, weber.san SUPER; knauf – Kbelosan J; Profi Plus – restoration plaster), we concluded that the thermal conductivity coefficient λ of mixture 6 shows several times lower value than the compared restoration mortars. We can therefore classify it in a group of restoration mortars with thermal insulating properties.

Another part of the experimental research will deal with determination of durability, study of porosity, degradation of the base walls after the end of the life cycle of restoration mortar based on polyurethane and determination of the drying potential.

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Sposób wykorzystania poliuretanu po zakończeniu jego cyklu żywotności

Streszczenie

Wykorzystanie surowców wtórnych stanowi bardzo istotny element w zakresie ochrony środowiska i przy zapewnieniu zrównoważonego rozwoju. Naszym celem jest stałe badanie ukrytego potencjału wykorzystania wytwarzanych odpadów. Oczywiście, zadanie polega na stałej optymalizacji sortowania surowców wtórnych i surowców mających na celu ich lepsze wykorzystanie, a ostatecznie na ich finansową wycenę. To jest nasz sposób reagowania na rosnącą potrzebę utylizacji odpadów i surowców odpadowych przed ich składowaniem, na które wpływa przede wszystkim określone, obowiązujące prawo dotyczące środowiska, a po drugie, ten krok jest częścią celów środowiskowych naszego społeczeństwa. Obecnie produkcja poliuretanów wynosi około 7% całkowitego wolumenu tworzyw sztucznych produkowanych w Europie. Republika Czeska ma roczną produkcję ok. 10 000 ton odpadów sztywnej pianki poliuretanowej. Są to głównie odpady wielkogabarytowe, które w zasadzie nie podlegają efektywnemu składowaniu. Powyżej podana masa/ilość odpadów poliuretanowych była inspiracją do zapoczątkowania badań podstawowych w zakresie wykorzystania recyklingu pianki poliuretanowej pod koniec cyklu żywotności produktu w segmencie materiałów budowlanych.

W artykule przedstawiono część wyników projektu badawczego pod nazwą „Badanie topografii powierzchni i struktury materiałów zdegradowanych przez sole i proponowane środki/zamierzenia (technologia odnawiania) za pomocą zapraw opartych na piankach poliuretanowych w końcu ich cyklu życia”. Są to: 1. eksperymentalne receptury zapraw renowacyjnych pochodzących z recyklingu pianki poliuretanowej o masie właściwej od 30 do 40 $kg \cdot m^{-3}$ i maksymalnej wielkości ziarna PUR 2 mm jako wypełniacza w zaprawach odnawialnych; 2. właściwości fizyczne i mechaniczne doświadczalnych mieszanek (masa właściwa utwardzonej zaprawy, wytrzymałość, czas rozsmarowania, przyczepność/stopień przylegania, kapilarna absorpcja wody, zawartość porów powietrznych); 3. opis stosowania odnawialnej zaprawy poliuretanowej na ścianie.