The evaluation of chosen properties of ashes created by thermal utilization of hazardous and communal wastes

***Waldemar Kępys*[1], *Damian Krawczykowski*[2] and *Tomasz Niedoba*[3]**

Hodnotenie vybraných vlastností popolčekov vytvorených tepelným spracovaním nebezpečných a komunálních odpadov

One of methods of the waste neutralization is their thermal transformation in suitable installations or devices in order to achieve the state, which is no longer dangerous for the human health and life or for the environment. In effect of the thermal transformation the "new" wastes are created, which, by law are suppose a to be utilized first. These wastes may be utilized if their properties are suitable. In the paper, the process of thermal utilization of hazardous and municipal wastes is presented, together with the investigation results of the grain composition, surface area, density and of the initial chemical analysis of the created ashes. The research of the grain composition was conducted by using the "Fritsch" apparatus. On the base of the grain composition, the surface area of ashes under investigation was determined, whereas the density was determined by using the helium pycnometer.

The purpose of the research was to determine how the properties of ashes are changed and if the differences allow to use these ashes in future.

***Key words**: communal wastes, hazardous wastes, wastes combustion, fly-ashes*

Introduction

The human activity causes more and more a production of creating wastes. If we do not want to leave many waste storage yards as "legacy" for the next generations, we must obey the rules of law (Dz. U. 2001, no 62, pos. 628).

First, we should prevent the formation of the wastes. If it is inevitable, we should ensure the possibly of their limitation and so the lowering their influence on the environment. Next, we must conduct salvage on them and at the end to neutralize the rests, finally by their storage.

One of the methods of the wastes' neutralization is their thermal transformation. There are many special installations or devices, whose purpose is to transform wastes to the state, which is no longer dangerous for the peoples' life, health and the environment (Polska Norma PN-Z-15009). The "new" wastes are being created as a result of this process, which also should be used as soon as possible or, if it is impossible, neutralized in the least harmful, for peoples and the environment, way. If such wastes may be used or not is determined by their properties. In the paper, the results of the grain composition, surface area and the density of the ashes created after hazardous and municipal wastes combustion were presented together with their initial chemical composition and chemical pollutants leaching.

The following methods were applied:

1. Granulometric analysis – laser method by using the Fritsch Analysette 22 apparatus.
2. Chemical analysis – by using the emissive spectrometer with the induced plasma PLASMA 40 (ICPAES) and the mass spectrometer with induced plasma (ICPMS) ELAN 6100 manufactured by PERKIN ELMER.
3. Density determination – helium picnometer Micrometrics 1305.

The main purpose of the research was to determine the properties of ashes created after combustion of municipal wastes and to answer the question how these properties are changed depending on the sort of the combusted wastes and the season when the wastes were combusted.

In the case of dangerous wastes, combustion plant, the composition of the furnace charge depends on the wastes caloric value. The charge is composed of many sorts of hazardous wastes, which are passed to the combustion so that the energetic value of 16 000 MJ/kg is ensured.

However, in the municipal waste combustion plant, the transported wastes are combusted after the decomposition of their incombustible part and the part assigned to composting. The wastes calorific value

[1] *Waldemar Kępys M.Sc.*, University of Science and Technology, Department of Mining and Geoengeenering, Faculty of Ecology of Mining Areas, kepys@agh.edu.pl

[2] *Damian Krawczykowski M.Sc.*, University of Science and Technology, Department of Mining and Geoengeenering, Faculty of Mineral Processing, Environmental Protection and Waste Utilization, damian.krawczykowski@agh.edu.pl

[3] *Tomasz Niedoba M.Sc.*, University of Science and Technology, Department of Mining and Geoengeenering, Faculty of Mineral Processing, Environmental Protection and Waste Utilization, tniedoba@isk.net.pl

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is about 6300 to 11700 kJ/kg and depends mainly on the season. The origin of these wastes is always the same.

The thermal process of hazardous wastes rendering harmless

The thermal utilization process of wastes (fig. 1) is composed from two basic elements. The first one is the hot part of the installation, the second one is the combustion cleaning system.

In the rotary furnace, the solid, semi-fluid and the fluid wastes are combusted. The length of furnace is 12 m and the external diameter is 3,2 m. The furnace is inclined by the angle 2° and the range of normal temperatures in furnace is 850° to 1100 °C. Wastes are combusted during 25 minutes to 1 hour. As a result of the combustion, the slag is created, which is passed to the wet slag trap. It is cooled there in water and transported to containers by scraper transporters. The gas products of the combustion in the rotary furnace are reheated in the reheating chamber, which is equipped with two burners of the power of 6 and 2 MW, as well as wash pipes adapted to the supplying high caloric fluid and gas wastes. The slag is carried to the wet slag trap and next to containers. Gases flow to the recuperatory boiler, where they are cooled to the temperature of 170-320°C. The boiler is producing the steam of the pressure 2 MPa and the temperature 270 °C in the amount of 12 Mg/h. The steam is then used for the technological and heating purposes and also to the electrical energy production in the turbo generator of the power of 1,6 MW. The last device of the hot part, as well the first one of the combustion cleaning devices is the electrical precipitator. Both, the recuperatory boiler and the electrical precipitator are equipped with the partially integrated fly ash carrying system (marked by the letter *C*), which occurs in the silo. The combustion is first cleaned from mercury compounds by the addition of Na_2S_4. As a result of the conducted reactions, hardly soluble salt HgS is created which is caught with dust remains and dust in the sack filter. This filter traps also dust remains and soles from the sputtering drier. The filter is equipped with a pneumatic system of dust draining to the special silos. Next, the combustion is cleaned in HCl and SO_2 washers and the remains of pollutants as dioxins, furans, PCB, acid components of gases (SO_2, HCl, HF), heavy metals dusts are removed by a filter with the active coal. The last stage of combustion cleaning is the catalytic decomposition of nitride oxides in the presence of a reducing medium (ammonia).

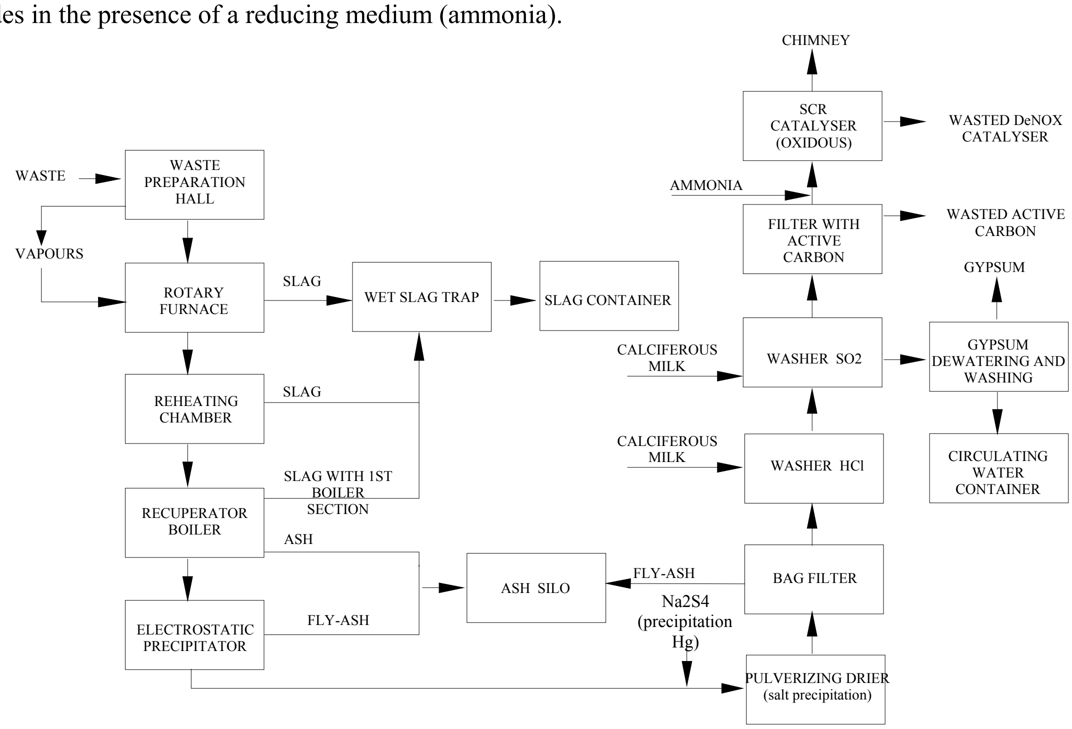

Fig. 1. Scheme of installation of hazardous wastes thermal utilization

Thermal process of communal wastes neutralization

The parts of technological process are:

a) acceptance of wastes with their weighing;
b) initial treatment of wastes;
c) combustion of energetic fraction, selected from the whole mass of communal wastes;
d) composting of organic material.

The installation scheme is presented on fig. 2.

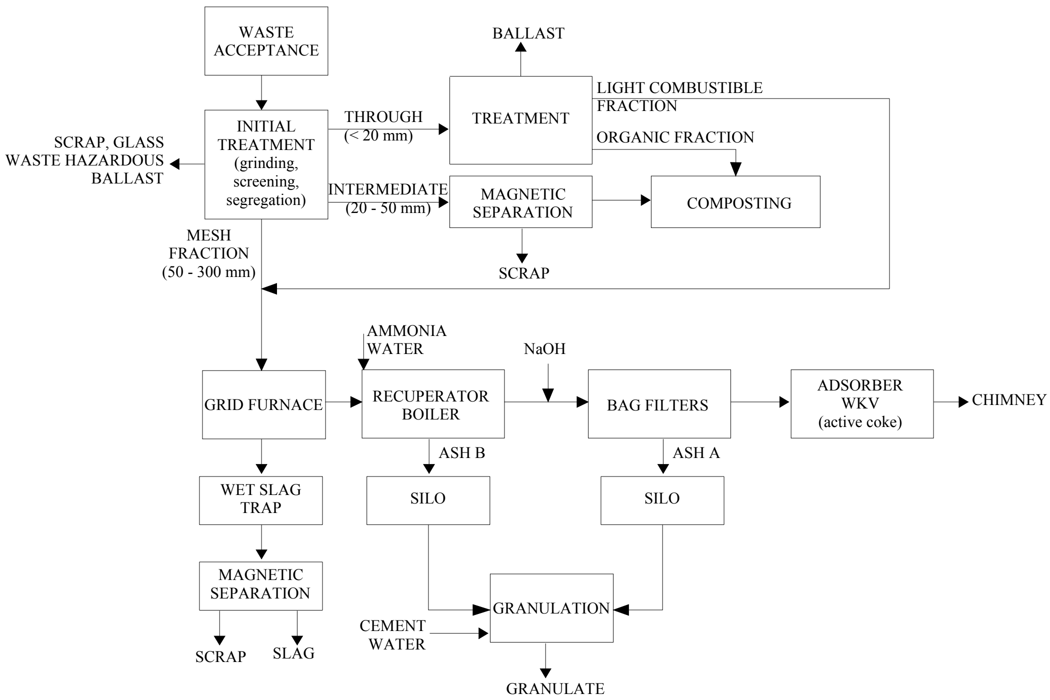

Fig. 2. Scheme of installation of municipal wastes thermal utilization

The municipal wastes are transported to the combustion plant by dust-free cars and after weighing are dumped to the moat. Then, the wastes are passed to the initial treatment, which is the segregation. In the first turn, they are sieved into two fractions – above and below 300 mm. Both these fractions are then segregated manually the glass (bottles), metal parts (the rest of them are caught by a magnetic separator), accumulators, hazardous wastes and ballast are being selected. After the segregation, the wastes above 300 mm are comminuted in beater mills and then sieved at sieves of meshes 20 and 50 mm. The heavy elements are ejected from the mill before achieving the comminution zone and occur in containers. They are the ballast ejected outside the combustion plant. The fraction below 300 mm is passed directly to rotary sieves. As a result of the sieving, three fractions are given, namely;

- 50 – 300 mm – which is passed to the combustion;
- 20 – 50 mm – which is passed to the composting, after ejection of metals;
- below 20 mm – which is treated on snaking tables and in cyclones. The selected organic fraction is then aggregated with the fraction 20-50 mm, the light combustible fraction is aggregated with the fraction 50-300 mm and the ballast is transported to containers.

The combustion occurs in the rotary furnace, inclined by the angle 25°. The temperature in the combustion chamber is maintained in the interval of 850-1150°C and the temperature in the reheating chamber is not below 950°C. The heat created in the combustion process is transformed into the electric energy, whose part is used by the combustion plant and the rest is sold, and the thermal energy, being used to heating.

The combustion cleaning is conducted in three stages:

1. No catalytic reduction of nitride oxides by the injection of warmed up ammonia water in front of the recuperatory boiler in the zone of high temperatures (about 950 °C).
2. Ejection of heavy metals' dust and acid combustion pollutants such as SO_2, SO_3, HCl, and HF on bag filters, by using powdered calcium hydroxide. The calcium hydroxide is inserted into the combustion collector and is passed to the four sections of bag filters with the combustions.
3. Reduction of dioxins, furans, heavy metals, aromatic hydrocarbons, ammonia contains in WKV adsorber with the active coke layer. The combustions are directed to the adsorber from the bottom side and flow in a stream, which is opposite to the moving adsorber layer.

The product of the combustion process is the slag, which after being cooled by water gives metals taken by using the magnetic separator and two sorts of ashes: ash from the recuperatory boiler (marked in this paper by the letter *B*) and the ash from the bag filters (marked by the letter *A*).

Description of the researches

As it was mentioned earlier, the grain composition, density, surface area, chemical composition and the chemical pollutants leaching were investigated. The research was performed on two samples from each ash.

The ashes were sampled five times from silos. In the case of dangerous wastes combustion plant, the samples (marked by the symbol *C*) were taken from the silo, where the fly-ashes from the electrical precipitator occur, the bag filter and the recuperatory boiler. However, in the municipal wastes combustion plant, features of ashes occurring in separated silos were investigated. These were ash es from beyond the recuperatory boiler – symbol *B,* and from bag filters – symbol *A*.

The numeric determination of the number of taken sample was added to the symbol, i.e. *C*-1, *A*-2 etc. Unfortunately, the sample *A*-1 was not taken at the first time (concerning ash from bag filters in the municipal wastes combustion plant).

The tab. 1 contains sorts of wastes, which were combusted before taking ash samples in the hazardous wastes combustion plant.

Tab. 1. The sorts of hazardous wastes combusted in the hazardous wastes combustion plant

Sort of combusted waste	**Percentage amounts of individual sorts of combusted wastes, being the source of created ashes**				
	***C*-1**	***C*-2**	***C*-3**	***C*-4**	***C*-5**
SOLID WASTES including:	70	65	40	30	68
- rubbers	-	+	-	+	+
- plastics	+	-	+	+	+
- tar sediments	-	+	+	-	+
- cleaner	+	-	-	-	-
- paper packages	+	+	-	-	-
- car upholstery	-	-	+	+	-
MEDICAL WASTES	30	35	25	---	13
PESTICIDES	--	--	20	45	19
SOLVENTS	---	--	15	25	--

Tab. 2. presents the months, in which the ashes samples were taken from the municipal waste combustion plant.

Tab. 2. The dates of ashes sampling ***from the municipal wastes combustion plant***

	Symbol of sampled ashes				
	***B*-1**	***A*-2, *B*-2**	***A*-3, *B*-3**	***A*-4, *B*-4**	***A*-5, *B*-5**
Month of taking ashes samples	Mars	Mai	October	Mars	July

The determination of grain composition, surface area and density

Tab. 3. Values characterizing the grain composition and physical properties of researched ashes

Sample	**Characteristic grain size**			**Density** [Mg/m^3]	**Surface area** [cm^2/g]
	d_{10} [μm]	d_{50} [μm]	d_{99} [μm]		
*A*2	3,11	11,86	169,67	2,290	4396,3
*A*3	3,42	16,91	257,59	2,196	3892,0
*A*4	4,78	32,19	367,17	2,446	2679,6
*A*5	3,58	18,56	325,32	2,298	3473,3
*B*1	14,54	152,0	883,24	2,608	540,4
*B*2	20,43	290,19	1051,14	2,604	391,2
*B*3	12,99	115,82	762,75	2,608	602,0
*B*4	22,51	184,40	1013,90	2,758	385,5
*B*5	16,58	163,80	850,99	2,710	472,1
*C*1	3,69	17,94	149,28	2,237	3787,9
*C*2	3,12	14,18	130,63	2,305	4336,7
C3	2,51	11,01	63,98	2,000	5975,9
C4	2,67	15,10	143,33	2,630	4111,3
C5	2,08	10,51	67,71	2,116	6594,7

The grain composition of analyzed ashes were investigated by the laser method, using the Fritsch Analysette 22 apparatus. Knowing the weighted yields of grain fractions of researched ashes, the surface area was calculated by using the equation (1) [Andreev 1959]. The density of ashes was determined by the Micrometrics helium pycnometer.The results of these analyses are shown in the form of grain composition curves Φ(*d*) in Figures 3-5, and the Tab. 3. contains a comparison of the characteristic grains *d* dimensions, density ρ of individual ash samples and their surface area S_{sit}.

$$S_{sit} = \frac{f}{A \cdot \rho} \sum_{i=1}^{n} \frac{\Delta \gamma_i}{d_{i_{sr}}} \qquad (1)$$

where: S_{sit} – the surface area [cm^2/g];

f – shape coefficient (for perfect solids *f*=6);

A – proportionality coefficient (for the percentage yields *A*=100);

$\Delta\gamma_I$ – yield of i^{th} grain class;

$d_{i_{sr}}$ - mean of i^{th} grain class borders [cm];

ρ - material density [g/cm^3].

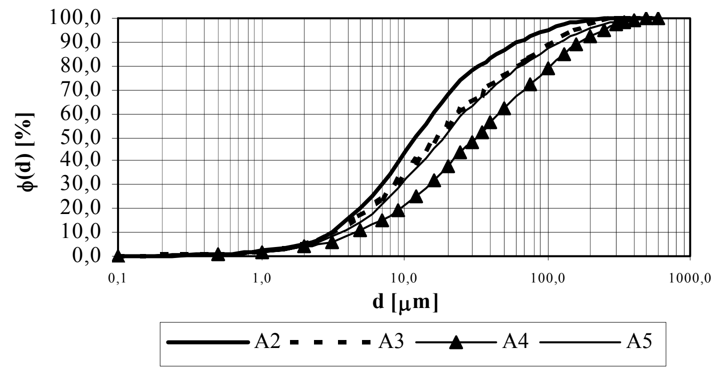

Fig. 3. Ashes' grain composition from bag filters in the municipal wastes combustion plant

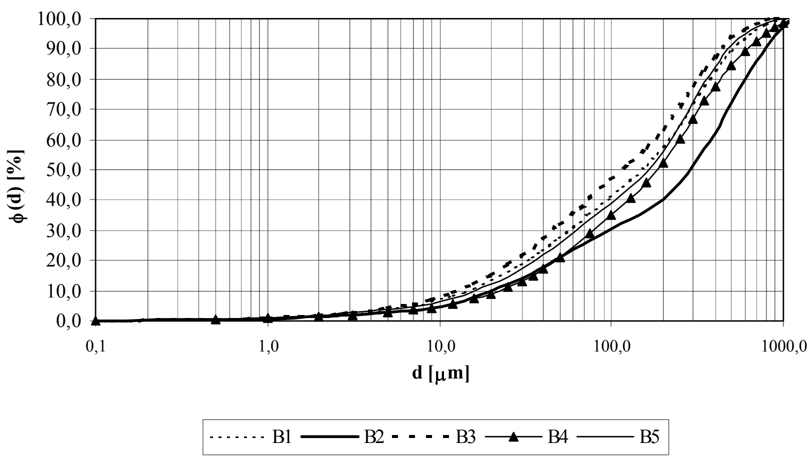

Fig. 4. Ashes' grain composition from beyond the recuperatory boiler in the municipal wastes combustion plant

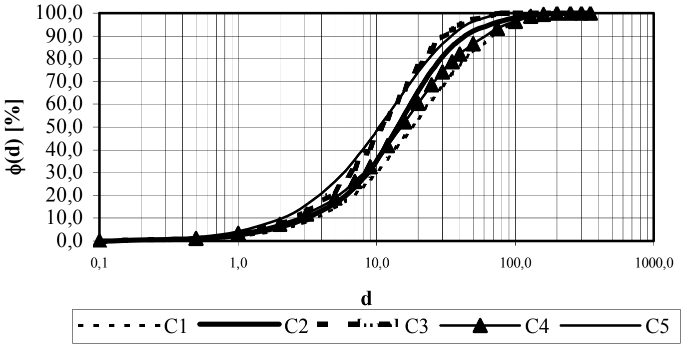

Fig. 5. Ashes' grain composition from the hazardous wastes combustion plant

It is clearly visible that the results for samples *A*, *B* and *C* are different even if we consider the samples from the same source. Certainly, the results of the surface area differ among the samples, which is caused particularly by the grain sizes. This fact may be crucial in the determination of certain ash properties. It can be difficult to investigate the exact characteristics of the ash as long as it is not fully recognized and its features are not easy to predict.

The chemical composition and leaching of chemical substances

As it was mentioned, the initial investigation of chemical properties was conducted. It rests on the investigation of the chemical composition and the leaching of every ash. Before the investigation the chemical composition, the ash samples were digested in the presence of HNO_3 at the temperature of 230 °C and pressure of 35 atmospheres. The water extract was prepared according to PN-Z-15009. The leaching and chemical composition results are presented in Tables 4 and 5.

Tab. 4. Leaching of chemical substances from researched ashes

Factor or sort of pollution	Unit	Ash *A*-3	Ash *A*-4	Ash *B*-3	Ash *B*-4	Ash *C*-2	Ash *C*-3
pH		12,44	12,45	11,94	12,0	6,95	6,66
Chlorides	mg/dm^3	16 477	16 985	1 630	1 963	8 723	24 930
Sulfates	mg/dm^3	762,3	4 017	6 161	3 145	1 025	893,2
Sodium	mg/dm^3	1834	1 982	2 062	1 091	1 337	4 323
Potassium	mg/dm^3	2 393,1	2 470	2 571	1 181	867,6	2 594,4
Zinc	mg/dm^3	17,64	15,4	0,084	0,071	202,2	648,9
Kadmium	mg/dm^3	0,887	0,00073	0,006	0,0089	5,69	8,44
Nickel	mg/dm^3	0,027	0,00117	0,00002	0,00108	0,269	0,34
Lead	mg/dm^3	168,6	70,36	0,66	0,164	2,288	15,31
Copper	mg/dm^3	0,701	0,155	0,016	0,002	1,188	0,461
Chromium	mg/dm^3	0,14	0,049	8,39	6,13	0,07	0,0055
Mercury	mg/dm^3	0,066	0,00091	0,0089	0,0014	2,68	0,986

Tab. 5. Chemical composition of researched ashes

Component	Ash *A*-3	Ash *A*-4	Ash *B*-3	Ash *B*-4	Ash *C*-2	Ash *C*-3
	[% weight]					
SiO_2	40,2	12,5	42,5	14,6	30,4	13,2
Al_2O_3	4,27	6,00	7,73	16,02	1,34	1,31
Fe_2O_3	0,79	0,77	1,26	1,98	1,46	1,31
CaO	37,83	56,63	23,58	46,08	32,29	37,6
MgO	1,27	1,29	2,02	2,50	0,76	1,48
K_2O	3,15	4,09	3,58	1,88	2,74	3,38
Na_2O	2,90	3,89	3,29	2,78	4,45	4,95
P_2O_5	0,51	0,40	0,88	1,44	0,18	0,27
ZnO	1,11	1,14	0,94	0,78	1,76	2,77
SO_3	7,08	8,45	8,71	11,32	9,47	23,02

The analysis of the chemical properties of the ashes was conducted on two samples from each sort of ash. A small amount of samples allows only to initially evaluate the ashes‘ chemical properties. It makes possible to recognize what sort of pollutants are leached and point out the big range of amounts of leached pollutants from all sorts of ashes. Only the values of ashes‘ pH were almost stable.

In the case of ashes *A*-3 and *A*-4 from the municipal waste combustion plant, it is visible that there is a huge leaching of chlorides, is (above 16 000 mg/dm^3), potassium (2400 mg.dm^3), of zinc (15,4-17,6 mg/dm^3) and of lead (70-168 mg/dm^3). The span for each of these pollutants does not differ between except lead, for which this difference is bigger. Big differences occurred in case of leaching of sulfates, cadmium, nickel, lead, chromium and mercury.

The ashes *B*-3 and *B*-4 are characterized by a less differential leaching but about 50 % or more significant differences occur in the case of sulfates, sodium and lead. The rest of pollutants as nickel, copper and mercury differ significantly but their amounts are vestigial. Furthermore, the contents of chromium is worthy to notice, which is about 6,13 to 8,39 mg/dm^3.

The big amount of chlorides from the ash *C* from the municipal waste combustion plant bag filters is leached, which is about 8 723-24 930 mg/dm^3. The other amounts are:

- zinc 202,2-648,9 mg/dm^3,
- cadmium 5,69-8,44 mg/dm^3,
- lead 2,288-15,31 mg/dm^3,
- mercury 0,986-2,68 mg/dm^3.

It is surely connected with the sort of combusted wastes given in Tab. 1.

The analysis of chemical composition show that the dominant components are SiO_2 and CaO and in their case the biggest fluctuations of their amount in every sort of ash occur.

Conclusions

The fly-ashes, which are the inconvenient wastes created in waste combustion plants are at the same time materials with properties allowing their using in many administration branches, as for example, the building materials industry. The properties of ashes and their application depend on many factors‘, from which the most important are (Giergiczny, 2002):

- sort of combusted waste,
- caloritic value and humidity of waste,
- method of waste comminution,
- furnace construction,
- method of catching the ashes from combustions stream,
- method of draining the ashes and conditions of their storage.

All of the factors mentioned above influence the chemical composition of ashes, as well as their physical features. After the elimination of the solid factors – which are typical for certain installation of wastes utilization – it occurs that the determining factor is a sort of combusted wastes, which is also decisive in their caloritic value and the humidity context. The conducted research showed that the properties of individual sorts of analyzed ashes differ significantly and are hard to predict, what determines the way of their utilization. The limited amount of researched ashes samples with respect to their chemical properties also show that the big span of chemical pollutants is leached out. However, in the case of chemical composition, it is more stable.

Because of so different properties of individual ashes, the possibilities of their application are very limited. It is connected surely with the necessity of transformation of these ashes into forms of stable physical properties, which also would allow to prevent chemical pollutants from being leached. One of these methods, allowing to use the ashes in a changed form in future is granulation with cement and media blocking chemical pollutants. It is applied for example in the municipal wastes the utilization installation presented in the paper.

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