Ashes from oily sewage sludge combustion: chemistry, mineralogy and leaching properties

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Tuhé produkty spaľovania olejových kalov: chemické zloženie, mineralógia a lúhovacie vlastnosti

Abstract: In the current paper the chemical and mineralogical properties of bottom ash and fly ash from oily sewage sludge combustion are investigated. The mineralogical composition and the morphology of ashes were determined by X-ray powder diffraction (XRD) in combination with scanning electron microscopy with quantitative energy-dispersive X-ray microanalysis (SEM-EDX). In addition, a leaching test results are presented to shed light on the potential toxicity of studied materials and their impact on the environment is discussed. Both of the studied materials are final products of thermal oxidation at industrial sludge incinerator. This facility aims to sanitary disposal of mechanical and biological sludge from industrial wastewater treatment plant. Bottom ash and fly ash are relatively stable solid products with slightly different chemical and mineralogical composition that reflects their different origin – burning condition in furnace vs. flues gas cleaning technology. Leaching tests of both mentioned materials were implemented under laboratory conditions. The aim of the laboratory tests was to determine the possibility of the pollutants release into the environment. The data presented herein support the importance of detailed mineralogical and geochemical study for the better understanding of the leaching tests. The obtained results showed that both of the sewage sludge ash samples exceed the criteria for accepting waste in landfilles established for Slovakia.

Keywords: bottom ash, fly ash, incineration, mineralogical analyses, leaching test, hazardous waste

1. INTRODUCTION

During the technological processing of crude oil, the emission of pollutants into the air and surface water together with the production of hazardous waste are known to have negative effects on the environment (Lynn et al., 2015; Xiao et al., 2015). Cleaning of chemically polluted wastewater resulting from the operation of petrochemical complex SLOVNAFT, Inc. Bratislava is ensured through the mechanical - chemical - biological waste water treatment plant (WWTP) and disposal of the resulting sludge (mechanical and biological) is ensured through internal sludge incineration plant. The WWTP and the sludge incinerator are located near the capital of Slovakia – Bratislava as a part of the refinery complex SLOVNAFT, Inc.

Sludge production

The mechanical and biological sludge is formed during the cleaning process of chemically polluted waste water from the petrochemical complex. The waste water treatment plant works in a three-step process – mechanical, chemical and biological, which controls the cleaning of industrial waste water. Treated waste water have to reach the limits (according to Annex No. 1 Act No. 364/2004 Coll., Anon, 2004) and could be further discharged into the Danube river. The by-products of cleaning processes are biological and mechanical sludges. In Tab. 1 the yearly production (2005–2014) of sludges is shown and Tab. 2 shows the chemical parameters of representative samples of mechanical and biological sludge burned in WWTP.

Sludge incineration and flue gas cleaning technology

The deposition of the sludge resulting from WWTP on agricultural land, land filling or incineration are some of the commonly used ways of the sludge handling processes in industry (Werther & Ogada, 1999). In our case, the thermal oxidation at sludge incinerator was used. The actual combustion process is supported by the addition of light fuel oil and natural gas with a slight excess of oxygen. In terms of legislation and waste management, handling bottom ash is classified under the Ministry of Environment Decree no. 284/2001 Coll. (Anon, 2001) as amended, as waste catalogue number 19 01 11 – ash and slag containing dangerous substances (category H – hazardous) and fly ash as 19 01 07 – solid wastes from gas treatment (category H – hazardous).

The sludge treated by combustion (about 20 % dry matter mixed sludge) inputs into the two technological units. The first technological unit is represented by a multiple-hearth furnace F5101 with eight floors where sludge gradually blows from the uppermost floor to the bottom one. Flue gases are released from the multi-stage furnace flues at the upper stage and enter the second – technological unit: the afterburning chamber F5202.

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Tab. 1. Yearly production of burned biological sludge (19 08 11*), mechanical sludge (19 08 13*), bottom ash (19 01 11), fly ash (19 01 07) and working time of sludge incinerator (*calculation on 100 % of dry mater).

Year	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Biological sludge [t]	1106	1083	1264	1448	1440	1475	1206	1129	821	834
Mechanical sludge [t]	2678	1692	2054	3049	2578	2043	2143	2202	1681	1768
Sludge Σ [t]	3784	2775	3318	4497	4018	3518	3349	3331	2502	2062
Bottom ash [t]	1338	760	1198	1655	1168	1189	1467	1277	965	1338
Fly ash [t]	121	71	381	514	755	615	590	581	487	634
Ash Σ [t]	1459	831	1579	2169	1923	1804	2057	1858	1452	1972
Working time [t]	7117	5163	6254	7244	6781	6228	5524	5673	4425	4971

Tab. 2. Total contents of potentially toxic elements, chemical parameters in representative samples of mechanical sludge (MS, waste catalogue number – 19 08 11) and biological sludge (BS, waste catalogue number – 19 08 13).

Parameters	DMC*	FluoridesTot	HalidesTot	ChlorineTot	N (V)	STot	As	B
Unit	% m/m	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
MS	32.02	6452	7.24	0.14	129	53890	50.9	418
BS	17.49	3484	1.38	0.086	338	10870	33.4	413

Parameters	Ba	Be	Cd	Cr	Cr (VI)	Co	Cu	Mn	Ni
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
MS	700	0.4	4.15	225	0.81	17.2	1410	428	344
BS	162	0.24	1.94	68.6	6.92	16.4	461	2840	139

Parameters	Pb	Sb	Se	Sn	Te	Tl	V	Zn	Hg
Unit	% m/m	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
MS	0.201	54.3	13.5	12.4	5.65	22.6	578	1.24	38.9
BS	0.045	34.9	78.3	8.81	1.71	29.4	206	6660	11.7

* Dry matter content

For elimination of combustible parts, the minimal temperature of 800 °C is reached in the oven, and flow conditions in the afterburning chamber are optimized by sufficient holding time (minimum of 2 seconds). The flue gas purification technology comprises the four following steps (Géci, 2013):

1. Selective non-catalytic NO_x reduction (SNCR)

During this process, the low concentration of flue gas NO_x is used. The reducing agent is injected into the flue gas in the afterburning chamber, where the optimal temperature required for the progress of denitrifying reactions is reached. The mixing of the reducing agent with the nitrogen oxides results in the decomposition of nitrogen oxides to elemental nitrogen and oxygen.

2. The dry flue gas cleaning (dry sorption)

For removal of acid components (HCl, HF, SO_x) from the exhaust gases, sodium bicarbonate is used as adsorption medium. The other adsorbent used is a mixture of zeolite and activated carbon. The dosage is controlled based on the concentration of the acidic components inputted to chimney. The neutralization and adsorption reactions take place in the pipeline system. Based on particular technological requirements, specific time is needed so that neutralization and adsorption reactions are completed.

3. *Membrane filtration*

The exhaust gases from the contactor contain a significant portion of solid particles, in particular fly ash from the combustion process, but also the particles formed during the gas cleaning process. Fine particles are composed of salts formed during neutralizing reaction and partially reacted sorbents - sodium bicarbonate, zeolite and activated carbon.

4. The catalytic decomposition of dioxins and furans

During the catalytic decomposition of dioxins and furans (abbreviated PCDD / PCDF) the catalyst V_2O_5 / TiO_2 is used. The catalyst is applied to the surface part of chemically stable non-reactive filter. Dioxins and furans in flue gas pass the filter and decompose to their constituent elements.

It is already well recognized that the samples of MSWI bottom ash are composed of:

- solid phases with high melting temperatures already present in the original municipal solid waste

– new phases formed during the high-temperature combustion process (Pfrang-Stotz & Schneider, 1995; Eusden et al., 1999).

The first group consists of refractories such as quartz, glass fragments, and metals, notably iron or steel. The second group includes predominantly two types of glasses formed from partial melts in the incinerator and their crystallization/decomposition products which are formed during cooling (Eusden et al., 1999), and unmelted glass shards. According to Eusden et al. (1999), the products of devitrification are melilite, magnetite and other spinels, together with plagioclase, feldspar, wollastonite and lime.

However, there are only relatively few studies focusing on the oily sewage sludge ashes using a mineralogical and geochemical approach. This information is necessary to develop an efficient pretreatment strategy of the ashes, prior to its utilisation or final disposal. Consequently, this paper provides information about metal contamination and the most important chemical, morphological and mineralogical characteristics of oily sewage sludge ashes (bottom ash and fly ash) arising as a result of disposal of oily sludges at sludge incinerator.

2. MATERIALS AND METHODS

2.1 Chemical analyses

For the purpose of this study two representative samples (0.5 kg each) of bottom ash and fly ash - were collected from the sewage sludge incineration plant. Particle size distribution was determined according to regulation STN722061:1985/Z1: 1997: Testing of fly ash for construction purposes. Determination of dry matter was carried out in a laboratory oven at 105 °C, followed by annealing in an electrical furnace at 550 °C to constant weight. The mass difference before and after drying was measured as a weight % of solids. Ash content (residue on ignition) was determined by calculating the value of dry solids and loss on ignition. The sulphate content in solid samples was determined by the chemical decomposition of the samples in the solution gravimetrically. The sample was decomposed by the action of HCl, afterwards $BaCl_2$ was added to the solution and then $BaSO_4$ was precipitated. The methods are based on the insolubility of $BaSO_4$ in water.

Metals were analyzed by atomic absorption spectrometry (AAS). Deuterium lamp was used to minimize interferences in flame injection solution. Laboratory blank solutions were running simultaneously to determine possible contamination. Light elements like oxygen and carbon were not analyzed.

2.2 Mineralogical analyses

Powder X-ray diffraction analyses (XRD) were conducted on diffractometer Philips under the following conditions: Bragg-Brentano geometry (Theta-2Theta), Cu anticathode ($\lambda\alpha 1$ = 1.54060 Å), accelerating voltage of 40 kV, and beam current of 40 mA. Ni Kβ filters were used for stripping of Kβ radiation on the primary and diffracted beam, and data were obtained using the PW 1711 detector. The step size was 0.01° 2Θ, the step time was 1 s per one step, and the range of measurement was 4–65° 2Θ.

Quantitative abundance of the main mineral phases in the X-ray diffraction patterns was determined by the Rietveld refinement with the program X'Pert High Score Plus. α-Corundum powder was mixed into each sample as an internal standard (0.25 g of standard was put into 1 g of sample).

Micro-characterization of the samples was performed in order to confirm and complete XRD results. Samples were examined by SEM combined with qualitative energy dispersive spectroscopy (EDS, TESCAN MIRA 3, EDX system by OXFORD INSTRUMENTS).

2.3 Leaching tests

Aqueous extracts of the ashes were prepared according to the EN 12457-4 protocol (2002). The standard describes a confirmatory test, which provides information on leaching of granular waste, at a ratio 10 L:1 kg of liquid to solid material with a particle size less than 10 mm. The method is suitable particularly for the examination of the inorganic components present. Preparation of water extract was performed at 20 °C ± 5 °C. The sample (0.090 kg ± 0.005 kg, dried weight) was placed in a bottle together with distilled water in a ratio: liquid to solid = 10 L:1 kg (relative tolerance ± 2 %). The bottles were shaken for 24 h ± 0.5 h. The sample was allowed to settle for 15 minutes. The extract was than filtered through a 0.45 μm filter using a vacuum filtration device. The filter residue was not washed with water or other solvent. The solution was analyzed for selected elements and anions respectively by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ionic chromatography (IC).

3. RESULTS AND DISCUSSION

3.1 Chemical composition of bottom ash and fly ash

The chemical compositions of the sewage sludge waste (SSW) ashes used in this work are summarized in Tab. 3. The bottom ash sample is characteristic by high amount of Fe and Ca, also significant is content of SO_4^{2-}, other elements such as Si, Al, Mg and Na are present in lower amounts. Fe and Ca account for approximately 23 and 20 wt. % in the bottom ash, while in the fly ash, the contents are only 3.49 and 2.94 wt. %, respectively. A significant enrichment of Fe and Ca in studied sample was observed, compared to the average composition of the continental crust according to Rudnick & Fountain (1995).

It is notable that studied sample of fly ash is rich in Na and SO_4^{2-}, amount of Fe, Si, Ca and Al is of lower significance (Tab. 3).

The high concentration of Na in ashes is attributed to the sodium bicarbonate used during the process of acid components removal and while Na and K belong to volatile elements, they show enrichment in the fly ashes (Li et al., 2004).

The fly ash sample has a higher Cl^- (0.7 wt. %) and F^- (4868 mg/kg) content compared to the bottom ash sample (Cl^- = 0.1 wt. %, F^- = 2933 mg/kg) probably due to the presence of $NaHCO_3$, which removes acidic gases such as HCl and HF

Tab. 3. Chemical composition of sewage sludge ashes from sludge incinerator. Total chemical composition is given in the form of element weight percents or mg/kg, independent of the actual form of chemical binding in the ashes.

	Bottom ash	Fly ash
pH	11.26	11.08
	% wt./wt	
LOI*	0.11	9.64
Dry matter content	99.85	99.64
Cl^-	0.1	0.7
SO_4^{2-}	11.47	30.39
Si	4.51	2.18
Al	4.97	1.35
Ca	20.06	2.94
Na	0.405	31.97
K	0.475	0.513
Fe	23.63	3.49
Zn	3.02	0.968
Mg	0.863	0.167
Mn	0.338	0.037
	mg/kg	
Cu	2100	328
Ni	870	109
Pb	2020	2550
Sb	<2	<2
Cr	385	81.8
Sn	301	189
Ba	2570	240
Cd	12.4	8.37
Co	42.8	3.62
As	130	66.6
Hg	0,38	15
Se	14.5	21.3
F^-	2933	4868

*LOI – loss on ignition

thus resulting in a high amount of chloride and fluoride content remaining in fly ash.

The high SO_4^{2-} content in fly ash with the concentration of 30.39 wt. % was detected. Sulfates and sulfides, together with Ca, K, Mg and Na, inhibit the stabilization of fly ash in cement materials. At the other hand, elements such as Ca, K, Na, Mg and Fe, can act as a molecular network improvers and are abundant in the ash, can help to break Si-O, Al-O bonds in quartz, silicates and aluminium salts and allow the formation of new silicates and aluminosilicates (Zhang & Zhao, 2009).

The chemical composition of ashes reflects the composition of the wastewater coming directly from the refinery complex, but also the wastewater (or liquid wastes), that are discarded by the WWTP coming from external suppliers. The main portion of Fe comes from external organization, where wastewater often contains up to 40 000 mg/l of Fe (total). Due to the significant fluctuations in the composition of the wastewater from external organization, the content of Fe in the ash can also widely vary and strongly depends on the composition of waste water.

During the incineration processes large quantities of ash containing considerable concentrations of potentially toxic elements (PTE) as well as trace amounts of organic pollutants are produced (Li et al., 2004; Jiang et al., 2007; Bayuseno & Schmahl, 2010; Bodénan et al., 2010; Chen et al., 2013; Lynn et al., 2015; Sormunen & Rantsi, 2015). The main PTE in SSW ashes include Pb, Cr, Zn, Hg, Cu, Ni, As and Ba (Tab. 3). Moreover, the concentrations of some potentially toxic metals and metalloids in the bottom ash are very high, such as Zn (30200 mg/kg), Cu (2100 mg/kg), Ba (2570 mg/kg), Pb (2020 mg/kg), Ni (870 mg/kg), Hg (0.38 mg/kg), Cr (385 mg/kg) and As (130 mg/kg). In the fly ash, the Pb (2550 mg/kg), Zn (9680 mg/kg) and Hg (15 mg/kg) concentrations were considerably high.

The volatilized PTE which leave the furnace could become a part of fly ash. The presence of different volatile compounds of these elements influences their final partitioning in bottom ash and fly ash. Some metals with high partial vapor pressures and low boiling points, such as Hg and Cd, are usually concentrated in fly ash, while other non-volatile species like Fe, Cu, Cr and Ni are mostly enriched in bottom ash. The presence of Hg and Cd in fly ash should be attributed to the carry-over of fly ash particles. The semi-volatile species (e.g. As, Zn) are likely to be present in both - bottom ash and in fly ash (Le Forestier & Libourel, 1998; Li et al., 2004; Sukandar et al., 2006; Xiao et al., 2015). Lead has either higher volatility or can easily form higher volatile chemical compounds and thus tends to be transferred into fly ash during the combustion process (Sukandar et al., 2006; Zhao et al., 2009).

In addition to inorganic pollutants, organic substances such as BTEX, PAH, PCB were also analyzed in the bottom and fly ash with concentration < 10 mg/kg, < 1 mg/kg, < 0.01 mg/kg, respectively. The content of hydrocarbons C_{10}-C_{40} was 106 mg/kg in bottom ash and 161 mg/kg in fly ash (data not shown in Tab. 3). Total contents of organic substances did not exceed threshold limits according to Anon (2015).

It is known, that pollutant concentrations in environment are dependent not only on the composition of MSW but also on the size of particles and flue gas treatment process (Le Forestier & Libourel, 1998). The particle size distribution in the ash samples showed that the bottom ash is more coarse-grained (the cumulative volume of the particles above 0.063 mm was 83 wt.%) than the fly ash (the cumulative volume of the particles above 0.063 mm was 21 wt.%) (Fig. 1a,b). Particle size distribution in ashes reflects the technological process of waste production. The handling process for both types of waste depends on the particle size distribution and chemical composition. Due to the coarser character of the bottom ash and its relative stability, this material can be directly disposed to the landfill for hazardous waste without further treatment. The finer fly ash must be modified before disposal into the landfill by the process of waste solidification. According to Chen et al. (2013), the fly ash should be more efficient material used as a cement

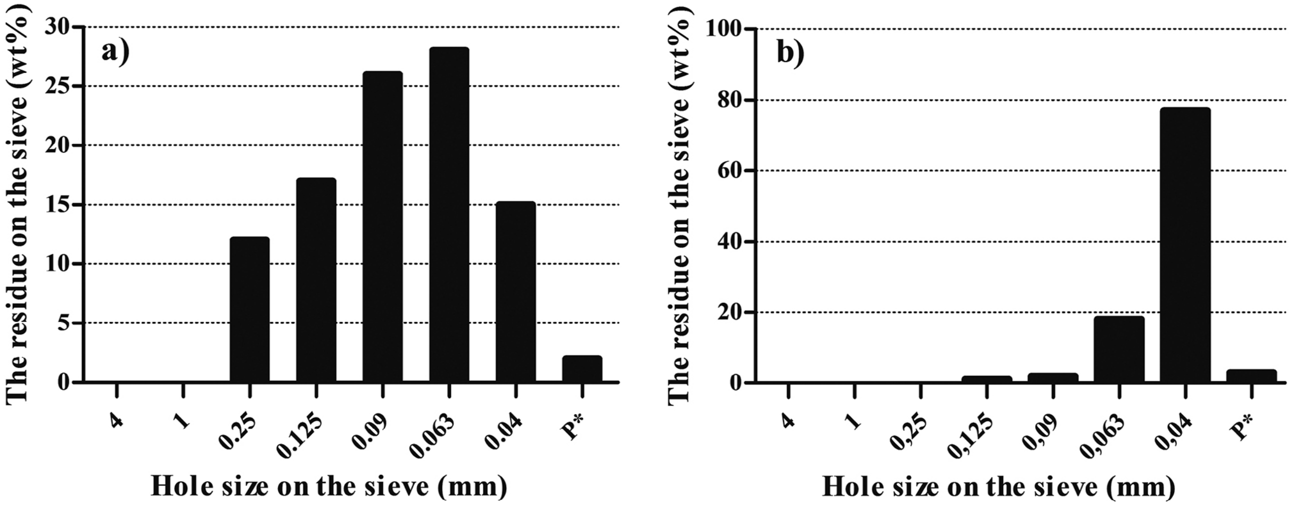


Fig. 1. Grain size of the bottom ash (a) and fly ash (b) particles.

addition agent because the finer particles would react more readily, and the hydration products would then crystallize at the close proximity of the particles. Therefore if ash is used as a substitute to cement, the smallest particles, which are reactive, would act as a binder whereas the biggest particles, much less reactive, would mainly act as a filler.

Loss on ignition is an important indicator for the evaluation of the amount of residual unburned organic carbon of the slag and combustion efficiency (Rocca et al., 2013). Compared to the bottom ash, the LOI of the fly ash was higher, above 9 %. The LOI values of the grate siftings (6.22 wt.%), the bottom ashes (11.17 wt.%, 15.53 wt.%), fly ashes (3.12 wt.%), the waste heat boiler ashes (3.60 wt.%) (Li et al., 2004), slag and fly ash from combustion of pelletized municipal sewage sludge (0.73, 2.08 wt.%) (Xiao et al., 2015), sewage sudge ash (1.3 wt.%) (Cheeseman et al., 2003), municipal solid waste ash (9.7 wt.%) (Kirby & Rimstidt, 1993) were commonly higher than those of the bottom ash (0.1 wt.%) in this study.

3.2 Mineralogical characterisation of the bottom and fly ash

A detailed knowledge of the minerals present in the bottom and fly ash together with their chemical composition is important in order to assess the relationship between microstructures and leaching behavior of the studied materials and to optimize the stabilized products.

According to quantitative XRD analyses the sample of bottom ash is composed mostly of Ca-Al silicate, gehlenite and Fe oxides such as hematite and maghemite (Tab. 4, Fig. 2). Dominant portion of hematite in similar samples was documented by numerous authors (Chimenos et al., 1999; Vassilev et al., 1999; Bayuseno & Schmahl, 2010; Bodénan et al., 2010). Other identified phases were graphite, wüstite and burkeite. Mineral phases such as mullite and ettringite were present just in trace amounts. The high background of the bottom ash XRD pattern indicates the presence of high portion of X-ray amorphous phases. According to SEM-EDS analyses these phases are composed mostly of various silicate glasses and unburned organic matter. The high content of glass in bottom ash samples was described by various authors (Zevenbergen & Comans, 1994; Pfrang-Stotz & Schneider, 1995; Bayuseno & Schmahl, 2010; Bodénan et al., 2010), as well as the presence of unburned organic matter (Chimenos et al., 1999).

Abbas et al. (2003) reported that a significant part of the cyclone ashes consists of silicates, aluminum-silicates and iron oxides. All these compounds have low solubility and can be expected to remain in the residue after washing.

The most commonly occurring mineral present in the fly ash sample was mullite (39.3 wt.%; Tab. 4, Fig. 3). High amount of X-ray amorphous material was present in the sample, mostly consisting of glasses with variable chemical composition (Tab. 4, Fig. 3). Phases like gehlenite, trona and burkeite were also commonly present (over 5 wt.% each). Fe oxides (maghemite and hematite) and anhydrite were present rarely (under 1 wt.%). This phase composition is in line with data published by Zhu (2011).

Tab. 4. Quantitative abundance of the main mineral phases in the bottom ash and the fly ash sample (wt.%).

Mineral	Formula	Bottom ash	Fly ash
Gehlenite	$Ca_2Al(AlSi)O_7$	13.3	8.4
Hematite	Fe_2O_3	12.0	0.4
Maghemite	γ-Fe_2O_3	11.5	0.4
Trona	$Na_3H(CO_3)_2.2H_2O$	0.0	7.4
Graphite	C	1.4	0.0
Wüstite	$Fe_{0.83}O$	0.8	0.0
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26(H_2O)$	0.1	0.0
Anhydrite	$CaSO_4$	0.0	0.3
Burkeite	$Na_6(CO_3)(SO_4)_2$	0.9	6.1
Mullite	$\sim Al_6Si_2O_{13}$	0.1	39.3
Amorphous phases		59.9	37.6
Total		100.0	100.0

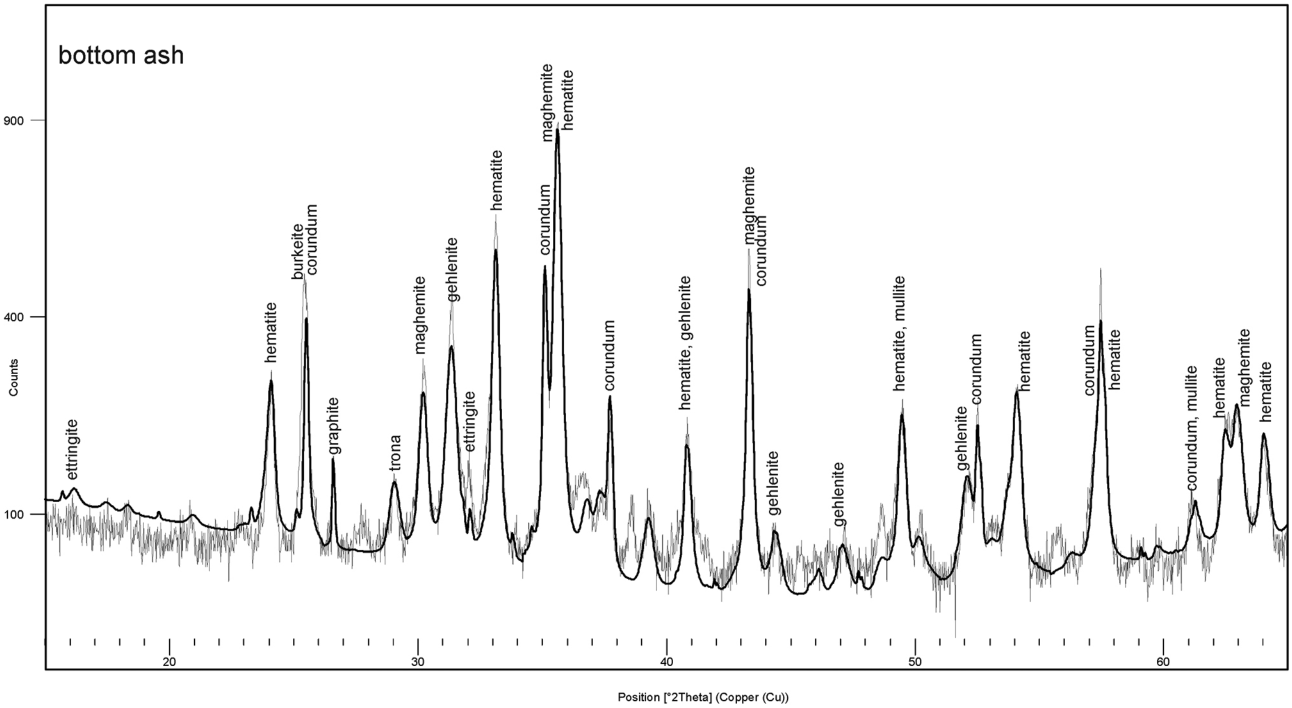


Fig. 2. Rietveld refined XRD pattern of bottom ash sample.

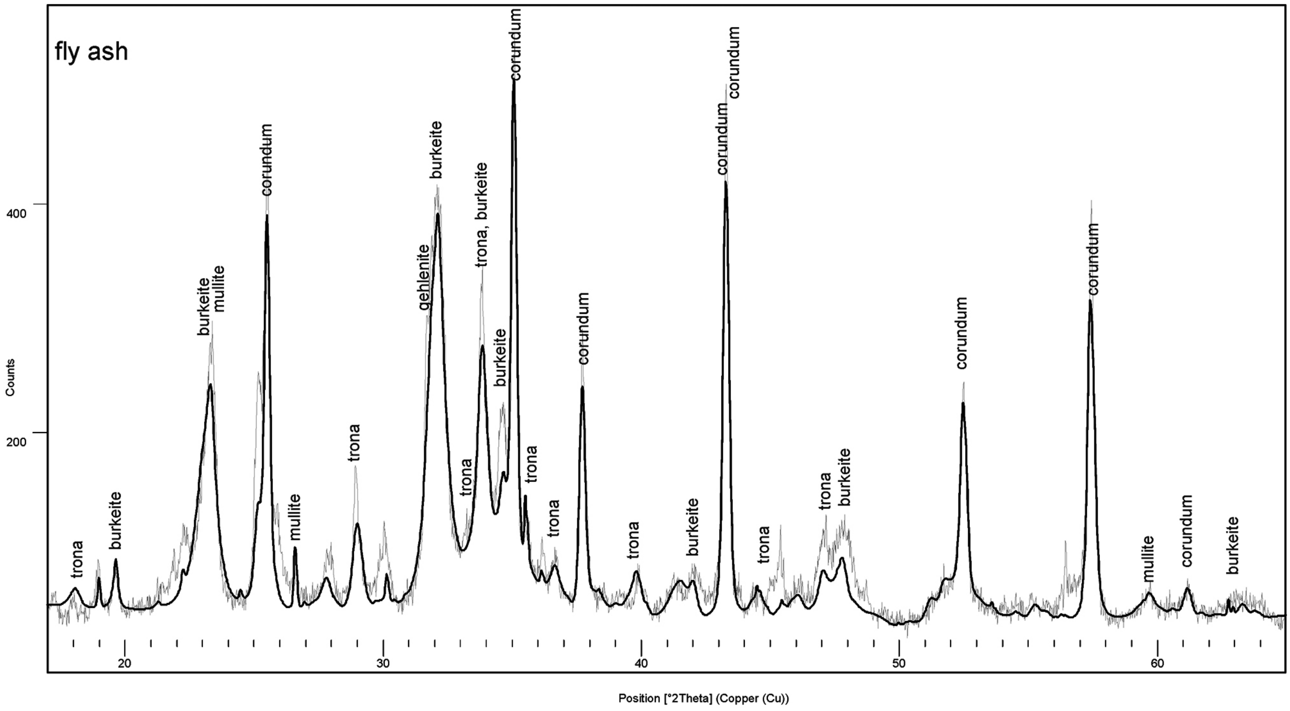


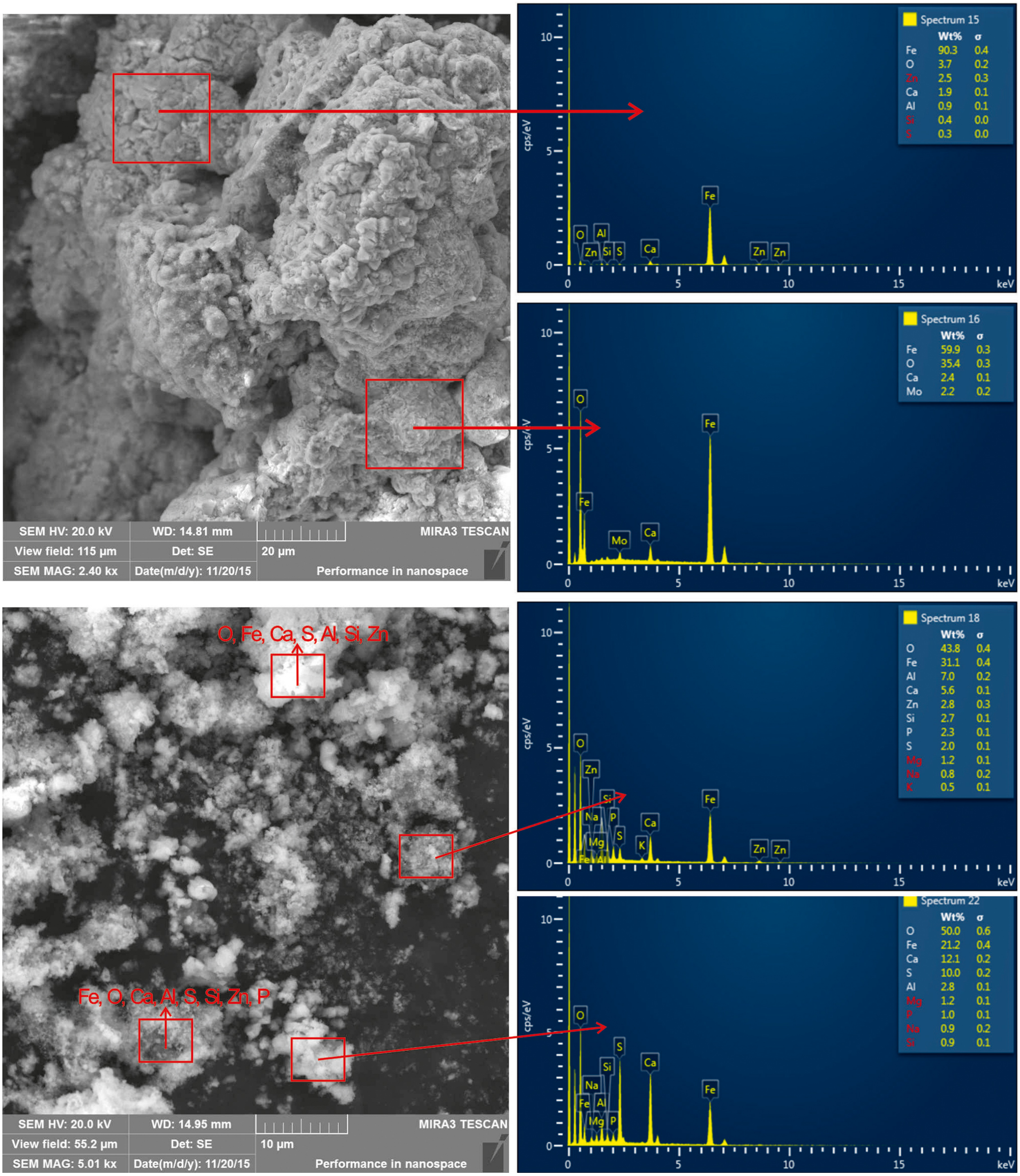
Fig. 3. Rietveld refined XRD pattern of fly ash sample.

Results obtained by SEM - EDS, agreed well with the results obtained by XRD (Figs. 4, 5). The most frequent phase in bottom ash are aggregates of amorphous particles with variable chemical composition, often rich in Fe, Al, Ca, S, with lower amounts of Zn, Si, P and S. Iron rich oxides occur frequently and are present mostly in form of aggregates of small crystals (from X nm to 5 μm large). The major part of the material is composed of porous particles, thermally fractured and the fractures originate from the escape of gases during combustion. Our results agree well with work of many other authors, especially Bayuseno & Schmahl (2010) or Bodénan et al. (2010).

In case of the fly ash, many well crystallized phases were observed in the scanning microscope. The most of them rich in Na correspond to trona and burkeite. Also common are well developed crystals of gehlenite. Amorphous aggregates are represented by phases with various chemical compositions, mostly containing Na, Si, S, Al, Ca, less of K, Fe, As, Mo and Cl.

The mineralogical composition of studied samples is in good agreement with the chemical analyses (Tab. 3). The high amount of Fe in bottom ash sample (23.6 wt.%) perfectly corresponds with the XRD results, according which Fe oxides such as hematite and maghemite are the main mineral phases (23.5 wt.%). Relatively high content of Ca is accommodated by gehlenite and ettringite; according to EDS results some portion of Ca is also incorporated into the glass particles (Fig. 4). SiO_2 is accommodated mostly by gehlenite, mullite and amorphous glasses.

In case of the fly ash sample, the main element present is Na (32 wt.%) and is incorporated into structures of trona and burkeite and some portion of Na is present in amorphous glass (Fig. 5). Sulfur is present dominantly as SO_4^{2-} in burkeite. SiO_2 and Al are present in structures of gehlenite and mullite, however significant portions of these elements are present in glasses.



Spectrum 15

	Wt%	σ
Fe	90.3	0.4
O	3.7	0.2
Zn	2.5	0.3
Ca	1.9	0.1
Al	0.9	0.1
Si	0.4	0.0
S	0.3	0.0

Spectrum 16

	Wt%	σ
Fe	59.9	0.3
O	35.4	0.3
Ca	2.4	0.1
Mo	2.2	0.2

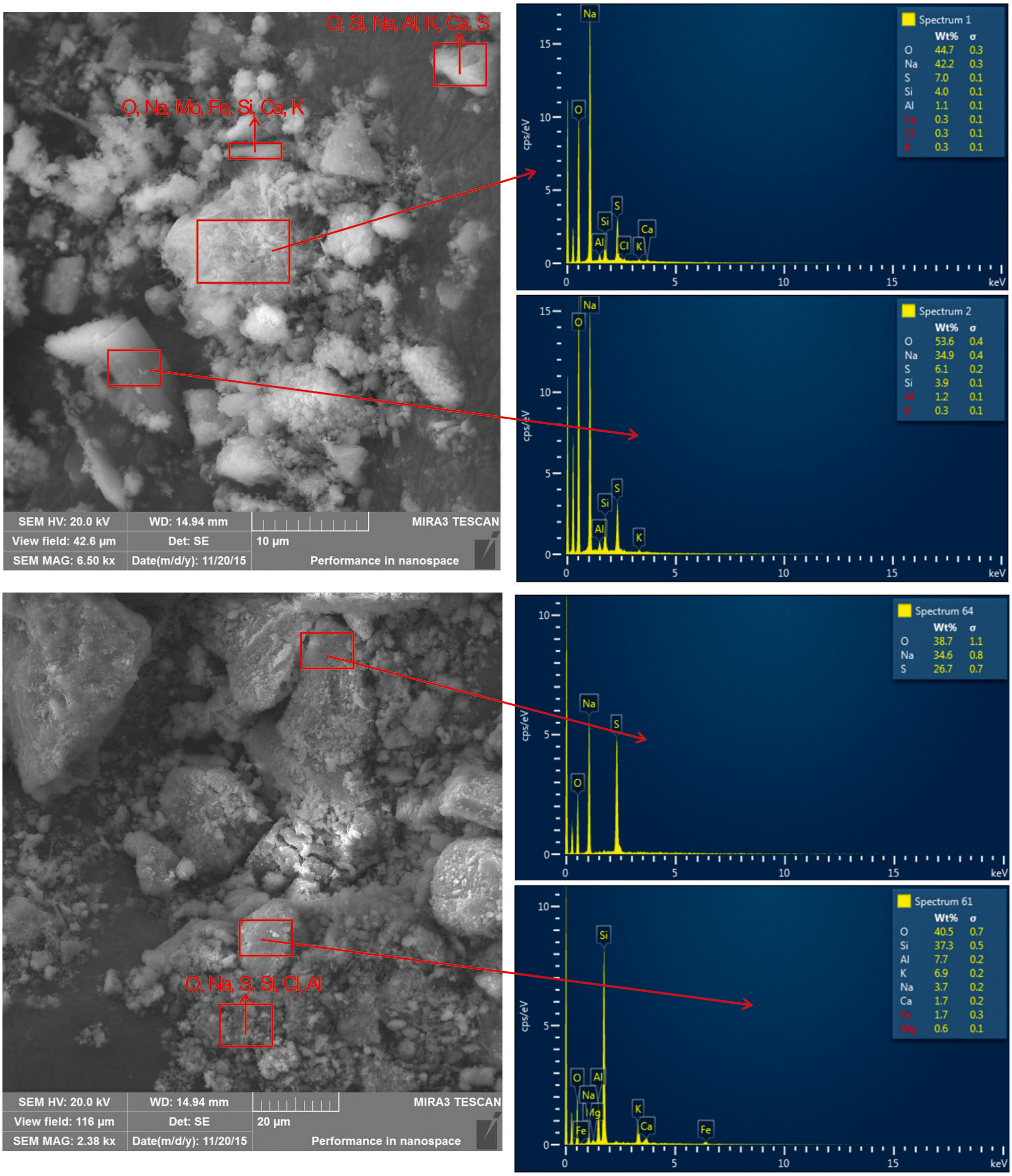
Spectrum 18

	Wt%	σ
O	43.8	0.4
Fe	31.1	0.4
Al	7.0	0.2
Ca	5.6	0.1
Zn	2.8	0.3
Si	2.7	0.1
P	2.3	0.1
S	2.0	0.1
Mg	1.2	0.1
Na	0.8	0.2
K	0.5	0.1

Spectrum 22

	Wt%	σ
O	50.0	0.6
Fe	21.2	0.4
Ca	12.1	0.2
S	10.0	0.2
Al	2.8	0.1
Mg	1.2	0.1
P	1.0	0.1
Na	0.9	0.2
Si	0.9	0.1

Fig. 4. SEM images of bottom ash sample with corresponding EDS analyses.



Spectrum 1

	Wt%	σ
O	44.7	0.3
Na	42.2	0.3
S	7.0	0.1
Si	4.0	0.1
Al	1.1	0.1
Ca	0.3	0.1
Cl	0.3	0.1
K	0.3	0.1

Spectrum 2

	Wt%	σ
O	53.6	0.4
Na	34.9	0.4
S	6.1	0.2
Si	3.9	0.1
Al	1.2	0.1
K	0.3	0.1

Spectrum 64

	Wt%	σ
O	38.7	1.1
Na	34.6	0.8
S	26.7	0.7

Spectrum 61

	Wt%	σ
O	40.5	0.7
Si	37.3	0.5
Al	7.7	0.2
K	6.9	0.2
Na	3.7	0.2
Ca	1.7	0.2
Fe	1.7	0.3
Mg	0.6	0.1

Fig. 5. SEM images of fly ash sample with corresponding EDS analyses.

The desired composition of the electrostatic precipitator ash entering an ash leaching system is low content of potassium and carbonate and high content of Na_2SO_4 which leads to the formation of a recycled ash mainly composed of Na_2SO_4. This is not always the case since the ash composition might vary significantly between mills (Jordan & Bryant, 1996). When the potassium content increases, K_2SO_4 starts to precipitate which leads to formation of the double salt glaserite ($3K_2SO_4{\cdot}Na_2SO_4$) (Goncalves et al., 2007). If the carbonate content increases, Na_2CO_3 will start to precipitate and form crystals together with Na_2SO_4, resulting in a double salt called burkeite ($2Na_2SO_4{\cdot}Na_2CO_3$) (Larsson, 2012).

The presence of trona in this type of ashes is very common, while sodium bicarbonate is used as adsorption medium for acid components removal from the exhaust gases (Pflughoeft-Hassett et al., 2009; Su et al., 2011; Wittenberg et al., 2013).

Based on other published data and chemical composition of ash samples studied in this work, presence of trace amounts of hydrocalumite, amphibole, muscovite, calcite, melilite, augite, chalcocite, alunite, potassium carbonate, halite, sylvite and portlandite, could be also expected (Bódenan & Deniard, 2003; Bayuseno & Schmahl; 2010; Bódenan et al., 2010).

In comparison with coal combustion ashes (Vassilev et al., 2003; Koukouzas et al., 2006; Kostakis, 2009; Font et al., 2010; Medina et al., 2010) the samples studied in this work are characteristic by lower amount of silicates and much higher content of carbonates and sulphates.

3.3 Leaching tests

The mineral assemblage of sewage sludge ashes are produced during high-temperature processes, therefore they are thermodynamically unstable under near-surface conditions. The incineration residues are highly reactive, especially under wet conditions. This means that the mineralogical and physicochemical characteristics as well as the leaching behavior of the sewage sludge ashes are changing as long as thermodynamic equilibrium with the surrounding environment is reached. Thus, change of the leaching behavior and contaminant release from these materials are influenced by the specific environmental conditions prevailing during utilization or final land disposal (Eusden et al., 1999; Sabbas et al., 2003; Bayuseno & Schmahl, 2010). Risk of PTE depends especially on the toxicity of solid products formed after treatment in WWTP. The ecotoxicity, bioavailability and mobility of PTE are determined by their chemical speciation and the leaching ability in MSS ashes rather than their total concentrations (Xiao et al., 2015). In order to assess the environmental impact of a waste material (mostly PTE), it is important to determine the total leachable content of PTE in this material.

During the contact of ashes with water, some elements such as salts and sulphates contained in glass compounds had tendency to be dissolved partly or completely. Generally the amounts of water-soluble forms of metals and metalloids in the ashes were low. Results of leachates are shown in Figs. 6 and 7, where they are compared to the threshold values for the different types of waste according to Anon (2015):

– Inert waste,
– Not dangerous waste,
– Dangerous waste.

The leaching tests conducted on the powdery form of sewage sludge ashes revealed that the concentration of the potential contaminants such as As, Mo, Se, fluorides, sulphates and total soluble matter were above the threshold limits considered in the Slovak regulation. In case of the bottom ash (Fig. 6), the concentrations of Mo (1.26 mg/l), Se (0.33 mg/l) and sulphates (2105 mg/l) in leachate exceeded the threshold values for not dangerous waste (Anon, 2015). Selenium water-soluble content exceeded guideline by 6 times. Among the studied elements, the highest values of water-soluble fraction in the fly ash was observed for Se (17.40 mg/l), fluorides (880 mg/l), sulphates (91800 mg/l) and total soluble matter (48210 mg/l), where the obtained concentrations exceeded the threshold values for dangerous waste and not dangerous value was exceeded in the case of As (0.66 mg/l) according to the Slovak regulation (Anon, 2015) (Fig. 7). The highest overrun of the limit concentrations were observed in case of Se, F and sulphates, 348-, 58- and 45-times, respectively. The leached amounts of Cd, Co, Cr, Cu, Hg, Ni, Pb and Sb in bottom ash and fly ash were lower than the detection

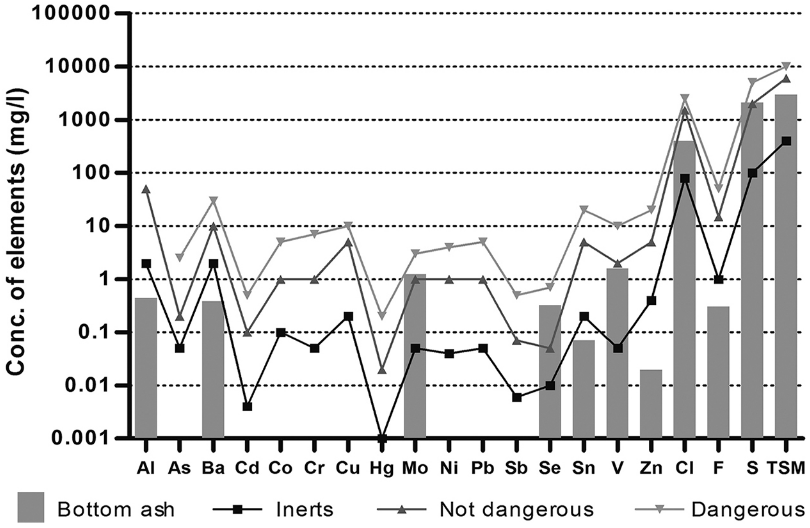


Fig. 6. Leached concentrations of selected elements after 24 h of agitation of the bottom ash compared to the threshold values for inerts, not dangerous and dangerous waste (Anon, 2015).

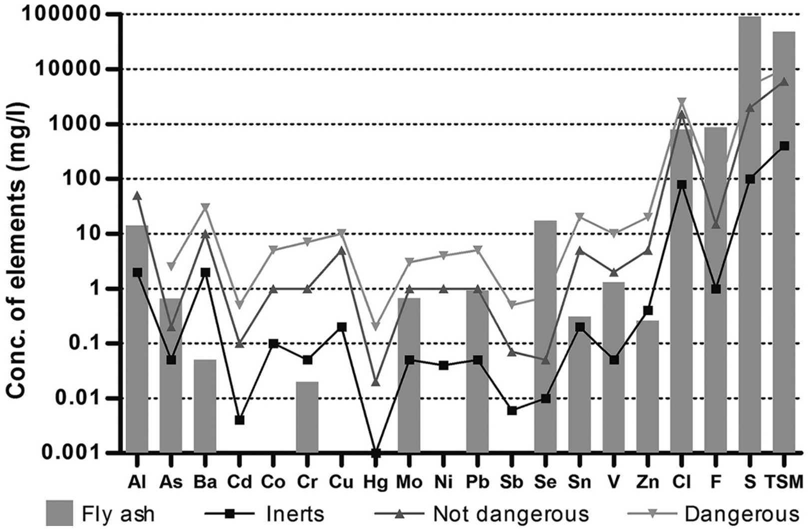


Fig. 7. Leached concentrations of selected elements after 24 h of agitation of the fly ash compared to the threshold values for inerts, not dangerous and dangerous waste (Anon, 2015).

limit of determination and these elements are not discussed further. Interesting is high Se solubility, although total contents of Se are relatively low, content in the leachates overrun limits for inert waste.

Of organic substances, only monohydric phenols with content < 0.03 mg/l in the bottom ash and 0.037 mg/l in the fly ash were analyzed in the leachates.

Ettringite, anhydrite and burkeite were probably most important phases controlling the solubility of sulphates. High water-soluble concentrations of Mo and Se from sewage sludge ashes are mentioned also in other studies. The release of Mo from these residues could be controlled by powellite ($CaMoO_4$) (Hyks et al., 2007). Donatello et al. (2010) reported that due to the high concentrations of soluble Mo and Se, the sludge ash that they studied was not suitable for disposal in non-hazardous landfills. Chen et al. (2013) found out that mixing of ash with cement and sand to produce mortar or concrete, induced a stabilization of Mo and Se and is a good treatment technology for these kinds of ashes.

According to Abbas et al. (2003), the bottom ash samples from combustion of MSW were mainly composed of silicate and aluminum–silicate minerals with low solubility. The fraction of soluble salts was low and thus, bottom ash with respect to the salts leachability can be considered as stable. In Xiao et al. (2015), fly ashes contained more exchangeable and carbonate PTE in comparison to slag. Therefore, the PTE in fly ash are more bioavailable and mobile than those in slag.

Sewage sludge ashes may be used as a good substitute to cement because of their similarities with cement material (Chen et al., 2013; Lynn et al., 2015). According to Chen et al. (2013), a water extraction process can remove the soluble salts present in municipal solid waste incinerator fly ash, which will help to increase the stability of the synthetic materials produced from the MSWI fly ash. The results of the analyses indicate that the milling process helps to stabilize the heavy metals in the milled extracted MSWI fly ash leading to the formation of a non-hazardous material with an increase in the specific surface area of about 50 times over that of ordinary Portland cement. According to Hyks et al. (2011), rotary kiln thermal treatment of bottom ashes can be recommended to reduce the leaching of Cu, Pb, Cl and DOC; however, increased leaching of Cr and Mo should be expected. Xiao et al. (2015) presented, that combustion of pelletized municipal sewage sludge is a promising technology for the enhancement of PTE immobilization and could serve as an effective way for the safe disposal of MSS.

The both, bottom and fly ash (modified by solidification) are disposed in controlled landfill for hazardous waste. Due to occurrence of easily extractable compounds (total soluble matter, chlorides, fluorides) in fly ash, its use as e.g. additive in concrete is unrealistic, but on the other hand this utilization seems to be suitable for the bottom ash.

4. CONCLUSIONS

To the best of our knowledge, there are just a few studies on the mineralogy and leaching properties of ashes from oily sewage sludge waters processed by mechanical - chemical - biological waste water treatment plant. A detailed characterization of samples of bottom and fly ash, collected at MSW incinerator located in Bratislava (Slovakia), was carried out in terms of chemical composition, morphology, mineralogy and leaching behaviour.

The fresh bottom ash consists mostly of amorphous phases (59.9 wt.%) and major crystalline phases are Fe oxides (hematite, maghemite) and aluminosilicates (gehlenite). The fly ash consists mostly of Al-silicates (mullite and gehlenite), amorphous and unknown phases, sodium sulphate and carbonates (trona and burkeite).

It was observed that Zn, Cu, Ba, Ni, Cr and As were enriched in the bottom ash, while Pb and Hg were enriched in the fly ash resulting from combustion of SSW. The results of leaching tests showed, that the concentrations of the analyzed potentially toxic elements were far below the threshold values limits with the exception of Mo, Se and sulphates in the bottom ash and As, Se, F^-, sulphates and total soluble matter in the fly ash.

The results of chemical analyses and leaching tests of the bottom ash and fly ash from combustion of oily sewage sludge demonstrate, that these ashes cannot be considered as inert waste and this has significant implications for their disposal and re-use. Both should be consider as hazardous wastes and a proper treatment must be done prior to landfill and disposal. Our results contribute to the development of adequate waste management strategies.

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