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Characterization of Solid Waste Materials from Municipal Solid Waste Incineration Facility

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ABSTRACT

The Municipal Solid Waste Incinerator Termizo in Liberec (Czech Republic) produces four types of solid waste materials intended to be used as components of cementitious materials. The ashes from coal power plants are well known as materials suitable for utilization as concrete admixtures but the waste materials from MSWI facilities are more variable in composition and properties. Elementary composition of the ashes was examined by X-Ray Fluorescence. Granulometry was determined by sieving. The morphology of the materials was studied by measurement of BET surface, Blaine specific surface, loose bulk density and real matrix density. These characteristics were found to be dependent on the point of separation of fly ash from the technology line. The enthalpy of hydration and pozzolanic activity was determined. The MSWI ashes showed significant differences between fly ashes collected at different points of the MSWI technology line, and comparison with published data revealed considerable differences in properties of ashes generated by particular facilities.

INTRODUCTION

Regulations on waste elimination make waste management a significant problem for the public authorities today. For a long time, the majority of waste was disposed of in landfills but this is now becoming impossible. The present time is characteristic by the tendency of maximal recycling of all types of wastes and reducing their disposal. Recycle approach to the waste treatment is absolutely superior when compared with other methods there were used till now especially from economical reasons. The directive of European Union No. 1999/31/EC imposes to the member states the obligation to reduce the total amount of damped waste. According to this directive, in 2010 the amount of disposed waste should be reduced to 75%, in 2013 to 50% and in 2020 to 35% of amount disposed in 1995. Separation and recycling of metals, paper, glass and plastics is well handled in Czech Republic but it is not enough to meet the above given requirements. The reasonable (and maybe the only) way to fulfill these requirements is to increase the importance of incineration of municipal and commercial solid wastes and to recycle the ashes produced by MSWI facilities. One of the promising ways is the application of MSWI ashes in civil engineering. The present paper deals with characterization of four types of ash generated by a modern MSWI facility from the point of view of their application in building industry as additives in cement-based composites. The general requirements on (coal) fly ashes for the utilization in concrete as pozzolanic active matter of filler are summarized elsewhere [Myška 2002].

Each MSWI plant generates several different kinds of ashes depending on the used technology but usually there is a bottom ash and one or more types of fly ashes which are/may be collected and separated at different points of flue-gas treatment system. The point of ash collecting determines its chemical composition, particle size distribution, content of heavy metals and toxic organic compounds etc. The relationship between the point of separation, its temperature and physical and chemical properties of the ashes in case of the Termizo plant was described elsewhere [Šyc et al. 2010]. Other important issue is the composition of the incinerated waste – it depends especially on the location and season. It means that the MSWI ashes – compared to the widely used coal ashes – represent much more complicated materials with place-to-place different and seasonally unstable properties.

EXPERIMENTAL

Materials

Four types of MSWI ashes were studied; the bottom ash (denoted S), the fly ash collected in 2nd and 3rd pass of boiler (A), the fly ash collected in 4th pass of boiler (B) and fly ash from the electrostatic precipitator (C); for more details about the MSWI technology applied in Termizo plant see [Šyc et al. 2010].

Methods

The chemical composition of ashes was estimated by X-ray fluorescence analysis (XRF) by apparatus ARL 9400 XP (Thermo ARL). The heat of hydration of fly ashes was measured by isothermal heat flow calorimeter KC 01 [Tydlitát et al. 2007]. The measurement was performed by mixing of 1 g of ash with 0.5 g of water; the heat flow was monitored for 48 h. The present values are averaged from two measurements. The particle size distribution was determined by standard grading analysis by set of sieves. The specific surface was determined by BET method (Sorptomatic 1990, Thermo). The real (matrix) density of the ashes was determined by helium pycnometry (Pycnomatic ATC, Porotec). Fineness was further characterized by measurement of specific surface by permeability method (Blaine method) [ČSN EN 196-6]. All the above characteristics are average of three determinations. The determination of pozzolanic activity was performed according ČSN EN 196-5. It is based on comparison of $Ca(OH)_2$ concentration in solution after contact of sample with saturated solution of $Ca(OH)_2$ (40° C, 8 days), with content of $Ca(OH)_2$ in saturated solution of the same alkalinity. The result of test has been determined on a graph – $Ca(OH)_2$ saturation isotherm – and the test is considered as satisfied (yes) when the concentration of dissolved $Ca(OH)_2$ in the solution is less than the concentration of saturated solution.

RESULTS AND DISCUSSION

Chemical composition

The approximate chemical composition obtained by X-Ray Fluorescence is presented in Tab. 1. in form of oxides. XRF is just a semi-quantitative technique and hence the present figures have to be taken into account just as indicative (error 20 % may be estimated). Unfavorable, from the point of view of concrete application, is especially high content of sulfates (SO_3)

and chlorides in fly ashes (A, B, C). They reduce the strength of concrete and promote the reinforcement corrosion. The sulfate content in the studied ashes is significantly higher than in common coal ashes. Similar content of sulfates was reported by [Gao et al. 2008] in MSWI fly ash from Hangzhou or by [Shi and Kan 2009] in Shanghai MSWI fly ash. The bottom ashes generally contain lower amount of SO_3 which was observed also in this work; but the reported SO_3 contents in a German [Miller and Rübner 2009] or Italian [Bertolini et al. 2004] MSWI bottom ashes were much more optimistic (0.7, 1.21 and 3.43 wt. %). The content of sulfates and chlorides can be decreased to a certain extent by washing out by water. The content of alkalis (Na_2O and K_2O) is high especially in fly ashes. Since the bottom ash contains certain portion of scrap glass there is a risk of alkali-silica reaction in the concrete containing the MSWI ashes. The desirable component is SiO_2 in "active" form – i.e. reacting as pozzolan with $Ca(OH)_2$ to binding products. The content of active SiO_2 can not be determined by chemical analysis but the pozzolanity must be tested separately.

The detailed speciation of particular elements in ashes might be theoretically clarified by X-Ray Diffraction (XRD) but it is not very helpful due to high content of roentgen-amorphous particles (especially in fly ashes) and high complexity of the system. Nevertheless quartz, calcite, anhydrite, gypsum and silicates may be expected. High content of chlorides in ESP fly ash indicates presence of soluble salts. The minor components of MSWI ashes are heavy metals and organic compounds.

The most promising chemical composition among the studied ashes has the bottom ash (S). It contains the highest amount of SiO_2 and Al_2O_3 but their concentrations were lower than in coal ashes. Moreover part of the measured concentration of "Al_2O_3" in bottom ash is due to metallic aluminium which is not separated within the MSW recycling system in Czech Republic. The aluminium metal is highly unfavorable component of MSWI bottom ash because of "aluminium-induced" hydrogen formation in alkaline environment in the hydrating concrete. The aluminium metal can be avoided by an alkaline treatment of the ash before the utilization.

Table. 1. Results of XRF chemical analysis.

	mass %			
	A	B	C	S
SiO_2	15.9	19.6	9.9	33.5
Al_2O_3	8.0	9.7	4.2	15.8
Fe_2O_3	2.9	3.4	1.9	8.4
CaO	25.7	25.6	13.0	19.4
MgO	2.1	2.4	1.2	2.0
SO_3	28.8	14.9	15.7	9.3
ZnO	2.8	2.5	8.0	0.8
Na_2O	5.4	5.9	17.9	3.6
K_2O	4.4	4.4	8.4	1.9
TiO_2	1.6	1.6	0.8	1.5
Cl	0.7	7.3	15.1	1.1
∑	98.1	97.5	96.0	97.1

Morphology and pozzolanic activity

The morphological parameters of the studied ashes are summarized in Tab. 2. The density is within the range typical for silicates. The other morphology parameters are highly dependent on the point of separation of particular fly ash (i.e. on the temperature prevailing there [Šyc et al. 2010]). The loose bulk density of particular ashes decreases with decreasing temperature of the ash separation; the ESP fly ash (C) is very voluminous which causes its handling to be very difficult. The value of BET specific surface is related to the reactivity of materials; it corresponds to the real surface of the sample, including the surface of pores. The measured figures are comparable with coal ashes. On the other hand the Blaine specific surface is a relative measure of fineness of the material; it should be close to the "geometrical", outer surface. It increases with decreasing separation temperature; the values for fly ash B and C are comparable to portland cement. The MSWI ashes, except the ESP fly ash, were found to be pozzolanic active.

Table. 2. Morphological parameters of ashes and their pozzolanic activity.

Ash	Matrix density	Loose bulk density	BET specific surface	Blaine specific surface	Pozzolanic activity
	kg/m^3	kg/m^3	m^2/g	m^2/g	
A	2730	820	2.22	0.17	Yes
B	2590	670	1.79	0.45	Yes
C	2640	310	1.37	0.87	No
S	2630	1180	1.50	0.08	Yes

The result of sieving is shown in Fig. 1. The bottom ash has the coarsest particles while the B and C fly ashes are the finest. [Shi and Kan 2009] published granulometry of MSWI fly ash from Shanghai. Its average particle size was 10 µm while the here studied fly ashes from Termizo have the average particle size over 100 µm. According to [Myška 2002] the desired granulometry of the fly ash for utilization as concrete admixture is finer than are the ones measured for MSWI fly ashes (Fig. 1.). The coal ashes from power plants usually fulfill this requirement. The particle size distribution of MSWI ashes can be improved by grinding but such operation is unfavorable for the economical reason.

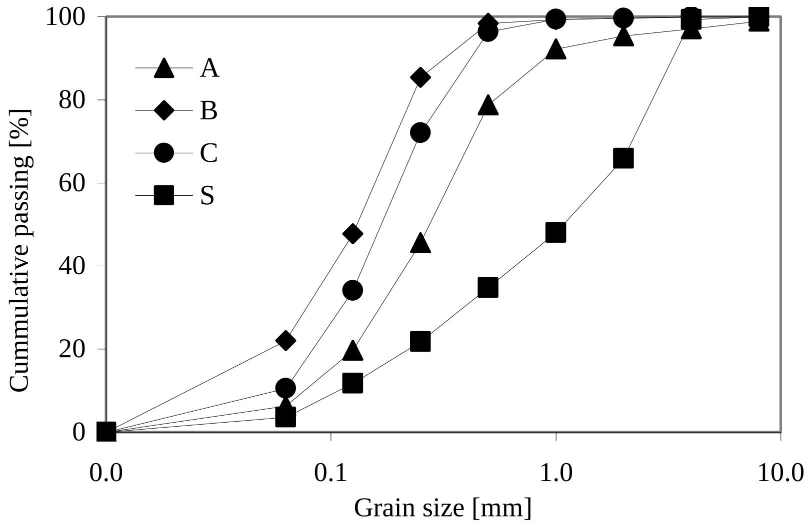

Fig. 1. Grading curves of the MSWI ashes.

Enthalpy of hydration

The hydration enthalpy of fly ashes was measured in order to describe their hydration process and to compare it with the ordinary portland cement (CEM I 42.5 R). The evolution of the heat output recorded for 2 days of hydration is shown in Fig. 2. The area under the particular curves corresponds to hydration enthalpy of the ashes.

Tab. 3. Hydration enthalpies of MSWI fly ashes.

Fly ash	Hydration enthalpy [J/g]		
	Total	1 h	2 - 48 h
A	134.0	19.1	114.9
B	59.4	19.4	40.0
C	205.2	27.7	177.5
Cement	237.4		

The shape of the curves provides information about the hydration process. The high heat output recorded immediately after the mixing of fly ash with water (up to 70 mW – not shown due to scale) indicates fast and exothermic hydration and subsequent dissolution of sulfates and chlorides. It includes also very fast hydration of anhydrite ($CaSO_4$) to hemihydrate ($CaSO_4.½H_2O$). The further hydration of hemihydrate to dihydrate ($CaSO_4.2H_2O$) is slower but it is completed within 1 hour. There is taking place also wetting of the ash particles but its contribution to the total heat output is just minor. Hence the "1-hour-enthalpy" caused by sulfates and chlorides dissolution was subtracted from the total measured enthalpy (Tab. 3.). The hydration heat generated after the first hour (2 to 48 hours) can be attributed to the hydration of silicates which results to binding products similar to CSH and CAH hydrates. The hydration enthalpy of portland cement is obviously the highest. The hydration of alit (C_3S) in cement to binding CSH is very fast hence it has no sense to subtract the first hour in this case. The "effective" hydration enthalpies (2-48 h) of MSWI fly ashes are lower than that of portland cement but they are measureable and prove the hydration process occurrence. Fly ash B provided the significantly lower hydration enthalpy than the other ashes.

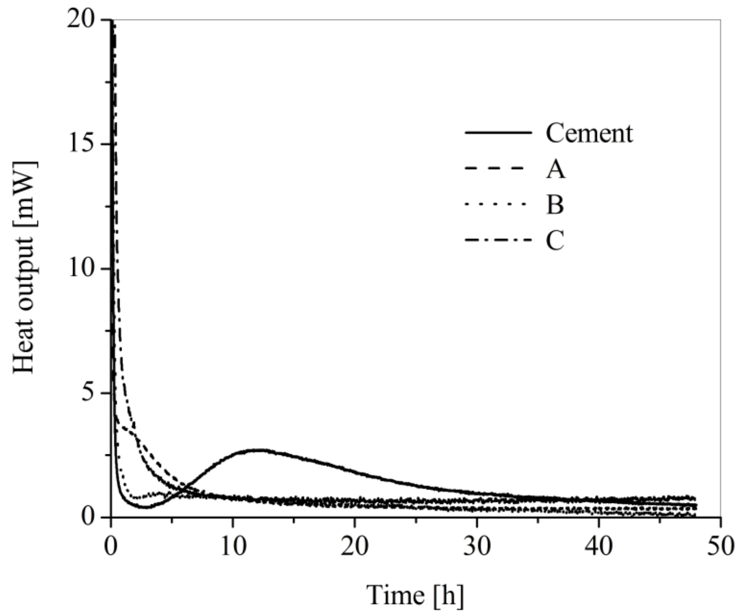

Fig. 2. Heat output measured during the hydration of MSWI fly ashes.

CONCLUSIONS

The four studied MSWI ashes from Termizo plant in Liberec differ significantly to each other. Since the MSWI ashes are intended to be used as a concrete admixture the chemical composition, their morphology and hydration were characterized. There are observable trends of their morphology in dependence on the point of collection and separation of the particular ash. The granulometry of MSWI ashes was found to be coarser than in case of coal ashes. The studied ashes contain high concentrations of chlorides and sulfates which are unfavorable in concrete. The bottom ash contains scrap glass and metallic aluminium which should be avoided in cementitious materials as well. On the other hand, the ashes – with one exception – were found to be pozzolanic active and certain hydration reactions of oxides were indicated; it means that the materials could contribute to formation of binding species in cement based composite materials. The question is whether the pozzolanic contribution to the cohesion of prepared cementitious material can compensate the negative effects of poor chemical composition and coarse granulometry. Some of these negatives may be suppressed by a chemical or thermal treatment (vitrification) of the ashes and subsequent fine grinding.

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