SOLIDIFICATION OF FLY ASH FROM MUNICIPAL SOLID WASTE INCINERATOR BY THE USE OF SOREL CEMENT

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Abstrakt: Spaľovanie tuhého komunálneho odpadu významne redukuje objem a hmotnosť tuhého komunálneho odpadu, avšak zvyšky po spaľovaní sú klasifikované ako nebezpečné odpady.

Použitím stabilizačnej technológie solidifikácie popolčeka z elektrostatických odlučovačov spaľovne na komunálny odpad využitím Sorelovho cementu vznikne popolčekový cement, ktorého environmentálne a inžinierske vlastnosti ponúkajú možnosť jeho užitočného využitia pre účelz stavebníctva.

Key words: Solidification, Fly ash, Sorel cement, Solid waste incinerator.

Introduction

Refuse incineration can significantly reduce up to 90% of the volume and 80% of the weight of municipal solid waste (MSW); however, the residues, bottom ash and mainly fly ash, often do not meet required standards for landfill disposal.

Of the two ash streams, fly ash having a large specific surface is the lighter, finer fraction, mostly in solid particle form, with some small or gaseous fractions entrapped in gaseous form. Fly ash is carried by combustion flue gas and then captured by air pollution control devices (electrostatic precipitator). Studies have consistently found fly ash to contain levels of heavy metals, dioxins, and other pollutants in excess of regulatory standards (Mahoney, 1988). Fly ash has a greater potential to adversely impact the environment than the bottom ash because it contains higher concentrations of some contaminants which are generally more sensitive to leaching as a result of the small particle size of fly ash.

Since fly ash contains a higher concentration of toxic elements than bottom ash, it is not usually possible to deposit it in ordinary landfills. The most common practice today is to combine bottom ash with fly ash at the MSWI facility and transport the combined waste to a disposal site. This practice diminishes the possibility of rendering an environmentally acceptable product as well as the possibility of utilizing ash residues. "The separation of fly ash from bottom ash and the direct controlled stabilization and landfilling of fly ash is a logical "first step" towards ash use." (Forrester, 1993)

Objectives

The overall objective of this study is to provide data for evaluating the leachability and physical characteristics of an ash-treated product prepared with a solidification technology by the use of Sorel cement. The secondary objective is to suggest the implementation of the new solid waste residue strategy for the municipal solid waste incinerators (MSWI). The treatment objectives are as follows:

1. To make waste acceptable for land disposal

2. To treat waste so it can be delisted (classified as nonhazardous) and disposed of at nonhazardous waste disposal facilites

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3. To treat waste so it can be utilized in the construction industry

The following steps were conducted to meet these goals:

1. Followed an ash residue sampling which is capable of providing representative ash samples

2. Stabilized the ash (according to a formula developed in a previous study) to produce an ash-treated product (i.e., ash-concrete product)

3. Quantified the leaching characteristics of heavy metals from the stabilized waste and from the waste itself

4. Determined the basic physical properties of the ash-concrete product unconfined compressive strength

The study program was carried out to provide the evaluation of the effectiveness of the solidification technology by the use of Sorel cement as a treatment process for fly ash from MSWI. The investigation objective was to emphasize the effectiveness of the treatment technology. Municipal incinerator design, operating conditions and waste input were not taken into consideration.

Sampling Procedure

Determining representative chemical and physical properties of fly ash and manufacturing of ash-concrete product requires collecting, screening, quartering, and testing enough sampless to assess the average properties of the fly ash and its variability. Analytical results from the fly ash analyses showed considerable variation in chemical composition. The main factors which influenced the chemical compositions were as follows: (1) differences in operating conditions at the municiapal solid waste incinerator at the time of sampling, (2) respresentativeness of actual sample collected, and (3) variable waste stream composition. Even though the samples undergo mixing and size reduction, any one sample can diverge from the average value representative of a particular fly ash stream from a MSWI. The ash sampling procedure followed was from "EPA Draft Sampling and Analysis of Municipal Refuse Incinerator Ash" issued on May 20, 1994, that incorporates accuracy and randomness into the sampling collection process.

The residues of fly ash were obtained during a single composite sampling event from the 250-ton-mass burn MSWI located in Rochester, Minnesota. The MSWI was equipped with electrostatic precipitators which were used as a particulate removal system. The sampling plan was chosen to obtain residues samples which, when combined into a composite, are representative of the overall ash stream. Representative is define as: The degree to which the data accurately and precisely represents a characteristic of population, parameter variations at a sampling point, a process condition, or an environmental condition (U.S. EPA, 1986, Test Methods for Evaluating Solid Wastes, SW-846, Method 1310, Second Editon). Sampling was performed by facility personnel during the third week of January 1995.

The following procedure was employed during ash sampling:

1. Collection of fly ash from the electrostatic precipitator was done at a fixed point from the fly ash pipe-line prior to exiting the incinerator.

2. Samples were taken each hour for a total of 8 hours.

3. The eight samples were placed into a container and composited into an 8-hour composite sample. The container was sealed, labeled, and stored for shipment.

4. Samples were collected each day over 7 days of facility operation in two shifts.

The information on the label included date, time of collection and sample number. Ash samples were then shipped to the laboratory where they were quartered to obtain a 1,000 -gram samples. The samples were then properly labeled and stored in plastic containers in a clean, dry, secure area. (ASTM Standard D 346).

Ash Composition

All fly ash samples were analyzed to specify their chemical composition. The elements analyzed in all samples were Zn, Pb, Cu, Mg, Mn, Cd, Al, As, Ag, Ba, Cr, Fe, Ti and V. Table 1 and 2 show results of chemical composition of fly ash for major and trace elements.

Table1.: Major components in samples of fly ash

	Data and Sample No.							
Component or element	01/23 1.	01/24 2.	01/25 3.	01/26 4.	01/27 5.	01/28 6.	01/29 7.	01/06* 8.
Major components [weight %]								
P	1.63	1.75	1.77	1.81	1.59	2.13	1.70	1.79
Ca	16.58	16.13	15.77	15.97	16.58	16.42	17.47	14.31
Ti	3.809	3.825	3.843	3.998	3.753	4.011	4.063	1.791
Fe	2.17	2.02	3.38	1.859	1.784	1.941	2.104	7.880
Mg	2.30	2.41	2.14	2.23	2.15	2.08	2.31	3.17
Na	6.42	7.12	7.64	7.35	7.20	7.46	6.24	2.44
K	4.43	4.59	4.95	4.90	4.80	4.80	4.23	3.81
Al	17.21	17.17	16.15	16.69	16.77	16.36	17.37	15.41
Si	22.17	22.47	21.17	22.28	21.91	21.95	22.03	35.82
Mn	0.11	0.11	0.12	0.09	0.09	0.10	0.11	0.22

*Fly ash sample from a MSWI in Košice, Slovakia

Table 2.: Trace elements in samples of fly ash

	Date and sample No.							
Component or element	01/23 1.	01/24 2.	01/25 3.	01/26 4.	01/27 5.	01/28 6.	01/29 7.	01/06* 8.
Trace elements [μg/g]								
Be	0.6898	0.6569	0.6078	0.5488	0.6129	0.6319	0.6084	8.8034
V	45.799	41.919	43.828	40.787	40.548	40.070	44.094	139.12
Cr	672.99	491.06	549.94	445.25	492.56	492.16	451.89	701.11
Co	22.027	17.333	17.742	17.667	15.889	20.328	17.463	29.105
Ni	171.93	175.18	118.90	87.630	100.95	224.176	135.89	113.91
Cu	626.25	713.61	882.23	624.62	634.76	846.60	753.52	645.57
Zn	17,940	19,320	21,580	16,070	18,810	17,940	18,390	10,180
Ga	32.916	32.691	30.284	32.113	33.587	31.076	31.473	23.032
Rb	57.703	57.742	61.041	59.414	60.826	58.703	55.021	89.467
Sr	240.91	219.51	226.44	232.82	237.43	251.96	245.66	460.50
Y	7.127	6.887	6.321	6.109	6.643	6.807	6.754	25.640
Ag	27.247	27.983	30.488	28.261	25.381	27.254	34.259	26.115
Cd	54.093	74.352	81.872	80.940	64.656	88.728	83.587	40.780
Sn	1423.8	1462.1	1543.9	1492.4	1650.1	1444.5	1511.4	916.39
Sb	1605.4	1808.7	1435.6	1431.3	2126.7	2796.4	2075.5	477.24
Mo	46.813	118.91	79.154	78.046	96.525	61.586	53.705	22.281
Zr	130.26	129.59	132.54	129.64	131.15	135.90	137.89	220.27
Cs	2.7058	2.6946	2.7832	2.6949	2.6938	2.6512	2.6826	13.456
Ba	784.42	613.77	1125.3	787.89	739.54	839.84	725.82	3439.8
Hf	3.0301	3.0141	3.0305	3.1437	3.0137	3.2112	3.2649	5.3704
U	1.5626	1.5386	1.7568	1.5264	1.5447	1.5436	1.6100	5.8968

	Date and sample No.							
Pb	2266.3	2719.6	2979.2	2348.5	2392.3	2523.2	2501.6	2313.2
Th	5.9739	5.4879	5.5169	5.6193	5.7373	5.6800	5.7721	10.043

*Fly ash samples from a MSWI in Košice, Slovakia

Stabilization of Fly Ash by the Use of Sorel Cement

The alternative waste disposal technique to landfilling the ash residue from a MSWI is to stabilize it by the use of the stabilization technologies available. The cement-based stabilization technologies are the processes in which the ash residue is mixed with cement. Stabilization refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form (Conner, 1992). Magnesia cement (Sorel cement) was used for the stabilization of fly ash from MSWI. Magnesia cement is the product resulting from an admixture of magnesium chloride, water and properly prepared magnesium oxide. Fly ash samples were mixed with caustic magnesium oxide (electrostatic precipitator fly ash from a magnesia processing plant in Slovakia) and magnesium chloride $MgCl_2$. 6 H_2O (Fischer Chemical, M33-500, No. 940527) and water according to formula developed in previous study (Mačáková, 1995) to prepare ash-concrete solid product. There was no calcium present in the components of magnesia cement. The mixtures were prepared at room temperature as follows:

1. Known weights of fly ash of each of daily samples and components of the magnesia cement were thoroughly dry-mixed in a bowl

2. Then the prescribed amount of water was added to the mixture

3. After all the liquid had been incorporated, the mixture was vigorously kneaded by hand for approximately 10 minutes

4. After mixing was completed, the mixture was cast into the cylindric plastic molds (2-inch diameter by 4-inch long) and cured at the ambient room temperature for one day

5. Samples of the stabilized ash-concrete product for each daily sample were prepared in duplicates

6. After 24 hours all samples, except four, were extruded from the molds and cured for 10 days at room temperature

Samples extruded from the molds were stiff, but wet on the surgface.Two duplicate samples from one day had not acquired sufficient strength to be extruded from the molds and two duplicate samples which incorporated fly ash from 01/25/95 were extruded from the molds with some destruction of the middle portion of the cylindrical shape . After the curing period, all samples were hard and dimensionally stable. The specimens were a homogeneous mixture of ash residue and Sorel cement. The fly ash was finely dispersed in the matrix with some occurence of clumps. Dimensional stability of the matrix was comprehended by linking of the particles present in the fly ash with components of Sorel cement. The clumps of waste were physically entrapped. The matrix presented porous characteristics. All testing on treated ash-concrete product and untreated fly ash was performed after completion of the stabilization to permit comparison of results.

Physical Testing of the Stabilized Waste Residue

For stabilized cement-like wastes, what ash-concrete product is, the testing of unconfined compressive strength provides useful information about:

- The ability of the stabilized waste to withstand overburden loads.
- The optimum water/additive ratios and curing times for cement setting reactions.
- The improvement in strength characteristics from the unstabilized to the stabilized waste. (Barth, 1990)

Unconfined compressive strength is a direct measure of the strength required to fracture a monolithic test specimen and is indicative of the load bearing capacity. The UCS was performed according to ASTM Method C-109. Detemination of UCS was made on each daily sample (2 inches in diameter by 4 inches long), following 10 days of curing ath the room temperature. The total number of samples was eight. A compressive axial load of 10 kN/V was applied to the molded cylindrical ash-concrete specimens using Compression Testing Machine. The machine had an upper and lower plate, and the sample was placed upright on the lower plate. The upper plate was lowered and brought into contact with the sample. Load was then added continuously. A sample failed when it reached its maximum compressive strength. Most of the samples fell catastrofically and lost their physical integrity by falling apart. The total load at failure was recorded for each specimen. The UCS is the ratio of the force applied at failure to the original cross-sectional area of the cylinder, usually expressed in pascals (Newtons/m^2) . The samples were tested by the same person to give the maximum precision in testing procedure. Table 3 lists the results of the compressive strength for the ash-concrete specimens in Mega Pascals.

Table 3: Unconfined Compressive Strength of Ash-Concrete Product

Sample No.	Diameter [mm]	Height [mm]	Area [mm^2]	Voltage [V]	Force [kN]	Strength [MPa]
1.	51.78	NA	2104.72	6.93	69.29	32.92
2.	52.16	97.46	2135.72	5.25	52.50	24.58
3.	50.74	95.06	2021.02	5.12	51.20	25.33
4.	52.76	91.72	2185.14	7.39	73.90	33.82
5.	51.44	92.46	2077.17	6.48	64.80	31.20
6.	52.31	98.05	2148.02	5.49	54.90	25.56
7.	52.20	98.04	2139.00	7.25	72.50	33.89
8.	52.04	98.16	2125.91	6.80	68.03	32.00

NA - data not available

The EPA considers a solidified material with a strength of 50 psi (pounds per square inch) = 0.344 MPa (MegaPascal) to have a satisfactory unconfined compressive strength (USEPA OWSER Directive, No. 9437.00-2A) to provide a stable foundation for materials placed upon it, including construction equipment and impermeable caps and cover material (3, p. 30). The typical construction and compaction equipments generate contact pressure of more than 1000 psi. The unconfined compressive strength for ash-amended product stabilized by the use of Sorel cement varies within the range of 3564 psi (24.58 MPa) to 4914 psi (33.89 MPa), thus offering satisfactory values for variable uses of ash-concrete product.

Leaching Characteristics

The main potential for contamination of the environment from ash-concrete product is considered to be leaching (through contact with infiltrating rain water or groundwater). As previously mentioned, the goal of stabilization is to achieve those physical-chemical changes that further reduce the mobility of the waste in the ash-concrete product. The potential for leaching is a function of the waste properties and the effectiveness of the solidification technology. To simulate the natural leaching process, the EPA developed the Toxicity Characteristic Leaching Procedure (TCLP). Although the current TCLP regulatory test , which was established by the U.S. EPA in November 1990, does not simulate leaching conditions in ash monofills or in ash-concrete product applications, it was selected as a leachability test for the purpose of the study. The main reason for using the TCLP was to obtain results that could be easily compared with existing TCLP results published for the fly ash treated by the different stabilization techniques.

Testing the leachability of the waste by the use of the TCLP assumes co-disposal of waste (MSWI ash residue) with MSW, specifically, the disposal of approximately 5 percent ash residue with 95 percent MSW or some other type of waste. The TCLP simulates what happens to waste when it is placed in a landfill and exposed to natural processes of MSW landfill, where through anaerobic decomposition of MSW an acidic leachate with a pH of approximately 5.0 is generated.

The TCLP specifies one of two extraction fluids to be used, depending on the alkalinity of the waste. Extraction fluid # 1 is prepared using the acetic acid and the strong base NaOH with pH maintained at 4.93 ± 0.05. This fluid is less aggresive and is used acidic wastes. For the purpose of our study the extraction fluid # 2 was prepared using acetic acid with pH maintained at 2.88 ± 0.05. Extraction fluid # 2 is more aggressive and is used on alkalinic wastes, like fly ash from MSWI. Destilled, De-ionized Water (DDW) was used to prepare the mixture of extraction fluid.

The acidity of the extraction fluid has an impact on the solubility of metals, especially lead and cadmium. If any one of the eight TCLP required metals in the sample exceeding the threshold limits, the material is classified as hazardous and should be handled as a hazardous waste.

The samples of waste were placed in a 2-liter bottle with the extraction fluid, and rotated in a rotary tumbler at 30 rpm for a period of 18 ± 2 hours. The extraction fluid # 2 (pH = 2.88) was selected because of the alkalinity of the samples and also to promote higher leachability for metals. Samples were prepared at a 20:1 liquid to solid ratio. One hundred grams of each sample and 2000 ml of the extraction fluid were placed in a HDPE bottles rotated in the tumbler. Three experimental levels within the TCLP procedure were conducted:

- The leachability of the untreated fly ash
- The leachability of ash-concrete product prepared by the use of Sorel cement and crushed by the determination of unconfined compressive strength
- The leachability of 100 gram-cylindrical samples of ash-concrete product.

After the 18-hours agitation period, the pH of all TCLP extracts were determined and are listed in Table 4. Extraction fluid was filtered using borosilicate glass fiber filters, which were acid-washed prior to their use (by rinsing with 1 N nitic acid followed by three consecutive rinses with DDW). All samples were then refrigerated and the metallic contaminants were determined. All results are listed in Table No. 5.

Leaching tests produce results, that are not directly applicable to leaching behaviour in the field, but numerous studies obtained by TCLP and EP Tox showed that TCLP is a precise test for the evaluation of metal contaminants in wastes.

Table 4.: pHs of all TCLP extracts

Sample No.	pH of fly ash EPS	pH of cylindrical samples crushed prior to their TCLP testing	pH of cylindrical samples
1.	6.55	NA	9.38
2.	6.55	NA	9.13
3.	6.48	9.64	8.43
4.	6.43	NA	9.20
5.	6.61	9.54	8.40
6.	6.22	NA	9.14
7.	6.96	9.59	9.05
8.	6.38	9.63	9.10

NA - data not available

The use of the inappropriate extraction fluid which would not simulate leaching conditions at an ash disposal site or natural conditions ash-concrete product will be exposed in beneficial use applications can alter the leachability of metals. Therefore the use of extraction fluid should be determined along with the conditions the ash would be exposed to. Nevertheless, the results of leaching tests combined with physical tests can be used as indicators of field performance and environmental impact.

The results of the TCLP test on stabilized ash-concrete cylindrical specimens, ash-concrete products on which compressive strength was applied and TCLP of fly ash are shown in Table 5. Results indicate that concentrations of As, Ba, Cd, Cr, Hg, Pb, Ag and Se (eight EPA- required metals) in fly ash stabilized by the use of Sorel cement were less than EPA criteria. The TCLP results for fly ash has shown that only concentrations of Se, Ba, Pb and Cd were above the detection limits for those contaminants. Se and Ba concentrations do not exceed the levels of EPA criteria. It is assumed that the Ba was brought to the mixture with the Sorel cement, because the concentrations of Ba in treated product are higher than the concentrations of Ba in fly ash.The Pb concentrations in samples of fly ash were slightly below the allowable level, but the Cd concentrations exceeded allowable level as much as 17 times. After stabilization, the concentration of Pb was decreased below the detection limit and the concentration of Cd was slightly above the detection limit. With the stabilization process, the Cd concentration was decrease more than 1,300 times. The stabilized ash-concrete product is, therefore, not a hazardous waste.

Table 5: TCLP results for fly ash and ash-concrete products

		Toxic element							
Date	Sample	As	Ba	Cd	Cr	Hg	Pb	Ag	Se
EPA	(ppm)	5.0	100	1.0	5.0	0.2ppb	5.0	5.0	1.0
01/23	fly ash	ND	0.40	**14.3**	ND	ND	**1.8**	ND	0.010
01/23	crushed*	ND	0.52	**0.0071**	ND	ND	**ND**	ND	0.010
01/23	cylinder**	ND	0.54	**0.0110**	ND	ND	**ND**	ND	ND
01/24	fly ash	ND	0.42	**16.7**	ND	ND	**3.0**	ND	ND
01/24	crushed	ND	0.53	**0.0092**	ND	ND	**ND**	ND	ND
01/24	cylinder	ND	0.38	**0.0067**	ND	ND	**ND**	ND	ND
01/25	fly ash	ND	0.44	**16.4**	ND	ND	**0.085**	ND	ND
01/25	crushed	ND	0.47	**0.0073**	ND	ND	**ND**	ND	0.012
01/25	cylinder	ND	0.47	**0.0056**	ND	ND	**ND**	ND	0.017
01/26	fly ash	ND	0.46	**17.4**	ND	ND	**2.6**	ND	0.013
01/26	crushed	ND	0.54	**0.0110**	ND	ND	**ND**	ND	0.010
01/26	cylinder	ND	0.42	<**0.005**	ND	ND	**ND**	ND	0.010
01/27	fly ash	ND	0.42	**17.5**	ND	ND	**2.3**	ND	0.016
01/27	crushed	ND	0.44	**0.0116**	ND	ND	**ND**	ND	ND
01/27	cylinder	ND	0.40	**0.0056**	ND	ND	**ND**	ND	0.011
01/28	fly ash	ND	0.48	**14.9**	ND	ND	**3.3**	ND	<0.010
01/28	crushed	ND	0.59	**0.0078**	ND	ND	**ND**	ND	ND
01/28	cylinder	ND	0.37	<**0.005**	ND	ND	**ND**	ND	0.010
01/29	fly ash	ND	0.46	**12.8**	ND	ND	**3.3**	ND	<0.010
01/29	crushed	ND	0.46	**0.007**	ND	ND	**ND**	ND	ND
01/29	cylinder	ND	0.43	<**0.005**	ND	ND	**ND**	ND	0.013
01/06	fly ash	ND	0.31	**10.2**	ND	ND	**1.9**	ND	ND
01/06	crushed	ND	0.65	<**0.005**	ND	ND	**ND**	ND	ND
01/06	cylinder	ND	0.82	<**0.005**	ND	ND	**ND**	ND	0.019

* ash-concrete product was crushed by the determination of UCS
** cylindrical specimens of the ash-concrete product without destruction

Evaluation

The treatment objectives were accomplished. As previously shown, the environmental and engineering characteristics of the ash-concrete product create the potential for its beneficial utilization. The fly ash treated by the use of Sorel cement to prepare ash-concrete product, can be delisted from the list of the hazardous wastes and disposed of at the nonhazardous waste disposal facilities and possibly even utilized in construction industry. The leaching tests should be repeated with the use of extraction fluid determined along with the conditions the ash-concrete product would be exposed to. Prior to the decision about beneficial utilization of the ash-concrete product prepared from MSWI fly ash certain qualifying criteria should be met: (1) there is no environmental regulation resticting the use of the product, (2) it is commonly available technology, material or engineering practice, (3) the product is of economic value.

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