

Fly Ash Treatment Technology in Modern Waste Incineration Plant

**Michal Šyc¹, Martin Keppert², Michael Pohořelý¹, Petr Novák³, Miroslav Punčochář¹,
Eva Fišerová¹, and Vladimír Pekárek¹**

¹*Institute of Chemical Process Fundamentals of the AS CR, v.v.i., Rozvojová 2, 165 02
Prague 6, Czech Republic, +420 220 390 372, E-mail: <šyc@icpf.cas.cz>, <gas@icpf.cas.cz>.*

²*Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech
Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic, E-mail:
<martin.keppert@fsv.cvut.cz>.*

³*MSWI TERMIZO, Inc., Tř. Dr.M.Horákové 571/56, 460 06 Liberec 7, Czech Republic.*

ABSTRACT

Current trends to reduce raw materials application lead to the idea of using solid residuals from municipal solid waste incineration (MSWI) plants in the construction industry in a similar way as solid residuals from coal-fired power plants. However, MSWI plant solid residuals are incomparably more heterogeneous than those of coal-fired power plants. Moreover, their environmental impact could be more dangerous due to the POPs and heavy metals content. Therefore, effective elimination of above-mentioned negative impacts is a prerequisite for further ash application.

Detailed description of MSWI plant technology equipped with fly ashes acid extraction for heavy metals wash-out will be presented. Composition of solid residuals, contents of minor and trace elements and physico-chemical properties will also be summarized in the study. Some trends of ash properties will be concluded, and the effect of MSWI technology and point of fly ash separation from flue gases will be discussed. layer for carriageways, mounds or backfills.

TECHNOLOGY OF MSWI TERMIZO

Technological line of the municipal solid waste incinerator TERMIZO (see Figure 1) consists of a combustion chamber with a stoker-fired furnace and with a post-combustion chamber with three vertical radiation passes and one horizontal convection pass. Ammonia liquor, 25 wt. %, is added into the upper part of the first vertical pass of the combustion chamber for selective non-catalytic reduction (SNCR) of nitrogen oxides. A power unit (steam boiler), a three-stage electrostatic precipitator (ESP), a catalytic filter (REMEDIA D/F Catalytic Filter System by W. L. Gore & Associates, Inc.) and a three-stage wet scrubbing system are situated downstream to the post-combustion chamber [Šyc et al., 2006; Pekárek et al., 2006]. In the first stage of wet scrubbing system (quench, HCl and HF absorption) proceeds shock cooling down of the flue gases by water from temperatures higher than 200 °C to about 65 °C take place, and also absorption of the gaseous acidic components, including some heavy metals (e.g. Hg, Cd, Zn, and Pb). In the second neutralization stage (SO₂ absorption and

oxidation) sulfur oxides are removed by the counterflow sprinkling of the flue gases with softened water with controlled doses of NaOH (pH adjustment to about 6). In the third wet scrubber stage dust and aerosols are removed by pressurized water in the course of the flue gases flow through a system of Venturi jets (so-called Ringjet).

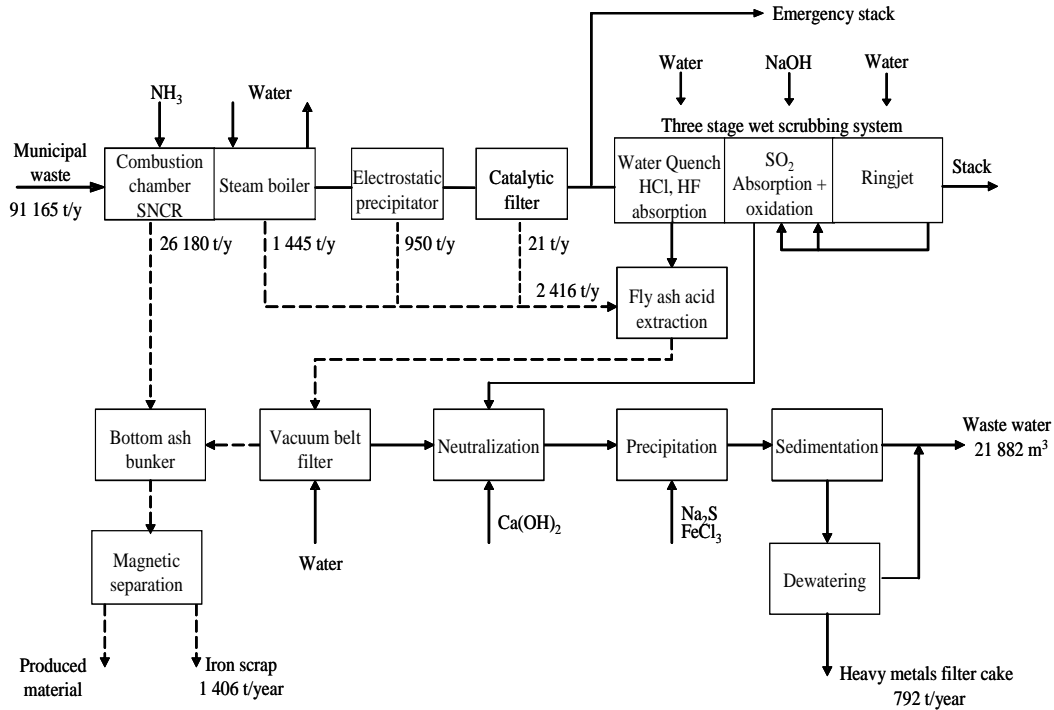


Figure 1 Flow sheet of MSWI TERMIZO (data from 2007)

In the MSWI Termizo fly ashes are stored in a silo and subsequently treated by a process called FLUWA. The FLUWA process consists in fly ash extraction by acidic technological water (pH \approx 3.5) from the water quench under higher temperature (ca. 70 °C) for minimum 45 minutes. Obtained ash suspension is separated and washed out by water on a vacuum belt filter. The filtrate, together with technological water from the second stage of wet scrubbing system, is neutralized by lime. Precipitation of heavy metals by means of Na₂S and addition of the FeCl₃ - flocculation agent at pH 9.5 under the formation of a flocculous precipitate are the subsequent steps. The precipitate is separated in a sedimentation tank, washed with water, and dewatered on candle filter in form of a filter press cake. The filter cake containing heavy metals is collected in special containers and disposed of on a hazardous waste landfill. Technological water from the ashes extraction and the remaining water from the wet scrubbing system are treated in a waste water treatment system. The cleaned technological water is discharged to a sewerage system. Bottom ash from the combustion chamber grate is cooled by passing through a water bath and stored in a bunker where it is mixed with acid extracted fly ash.

Furthermore, produced dewatered filter cake can be potentially used as a raw material for recycling Zn and some other metals. By above mentioned process of acid extraction of fly ashes it is possible to remove the following amounts of heavy metals: Cd \geq 85%; Zn \geq 85%; Pb, Cu \geq 33%; Hg \geq 95% [European Commission, 2006]. The Swiss company Von Roll is the supplier of the described technology. A similar technology is installed in more than ten

European incinerators. Moreover, the acid extraction technology FLUWA mentioned above is the best available technique (BAT) for ashes processing [European Commission, 2006].

Generally, solid residuals from combustion process could be divided into bottom ash and fly ashes. Moreover, fly ashes could be subdivided into more fractions on the basis of point of separation from technological line. In the MSWI Termizo, there is:

- fly ash collected in the power unit (steam boiler),
 - in the 2nd and 3rd pass of boiler (collected at temperature higher than 700 °C),
 - in 4th boiler pass (700–500 °C),
- fly ash from the three-stage electrostatic precipitator (500–250 °C) and
- fly ash from the catalytic filter (200–250 °C).

However, fly ash enters the acid extraction process as a mixture of above mentioned fractions. Annual production of solid residuals in the MSWI Termizo in the year 2007 is shown in Figure 1.

ASH PROPERTIES AND COMPOSITION

The character of solid residuals from combustion is predominantly determined by two factors. The composition of incinerated wastes is the first one. Incinerated waste composition depends partially on the given season of the year; substantial differences are connected with the geographical location of the incinerator. The second factor affecting solid residuals character is the point of separation from flue gases. Character, composition and the POPs content are also substantially influenced by technological line of given incinerator.

Physicochemical properties of ashes are presented in Table 1. The solubility tests were done at liquid to solid ratio (L/S) 10:1 at a room temperature, the pH of ashes was determined in distilled water at L/S 10:1 as well. Loss on ignition (LOI) was determined by heating at the temperature of 550 °C for 6 hours.

Table 1 Physicochemical properties of fly ashes

| | Bottom ash | Boiler 2 nd , 3 rd pass | Boiler 4 th pass | ESP | Catalytic filter | Fly ash mixture |
|---------------------------|------------|---|--------------------------------|-----------|---------------------|--------------------|
| pH | 9.3 ± 0.5 | 12.1 ± 0.5 | 11.9 ± 0.5 | 6.6 ± 0.5 | 6.2 ± 0.5 | 11.7 ± 0.5 |
| LOI (wt. %) | 1.2 ± 0.2 | 2.6 ± 0.3 | 3.9 ± 0.3 | 2.2 ± 0.2 | 1.5 ± 0.2 | 2.0 ± 0.2 |
| LBD (kg m ⁻³) | 1180 ± 150 | 820 ± 100 | 670 ± 100 | 310 ± 70 | 190 ± 50 | 650 ± 100 |
| Solubility in (wt. %) | | | | | | |
| Distill. water | 10 ± 3 | 14 ± 3 | 16 ± 4 | 51 ± 7 | 60 ± 7 | 23 ± 5 |
| HCl (pH=3.5) | - | 15 ± 3 | 16 ± 3 | 47 ± 6 | 50 ± 5 | 22 ± 5 |
| HCl conc. | 30 ± 3 | 52 ± 5 | 51 ± 5 | 79 ± 5 | 87 ± 5 | 59 ± 5 |

LOI - loss on ignition; LBD - loose poured bulk density; fly ash mixture - mixture of all fly ashes fractions

The LOI value of bottom ash is determined principally by the amount of unburnt carbonaceous residue. In the case of fly ashes, the LOI should be ascribed to chemically

bound water and to volatile substances condensed on fly ash. The LOI value of bottom ash 1.2 wt. % means that MSWI TERMIZO could be rated among modern incinerators.

Alkaline pH values were found for bottom ash, both boiler fly ashes and for the mixture of fly ashes. Fly ash from the ESP and from the catalytic filter is neutral or very weakly acidic. The alkaline pH values are given by the high contents of alkaline components in ashes. The neutral or weakly acidic character was found for fly ashes with the longest residence time in flue gases separated at lower temperatures. Along with their composition acidobasic character of fly ashes is given by the so-called sulfation, i.e. by the amounts of adsorbed SO₂ that is given by the contact time of the flue gases and ashes and by the flue gases temperature [IWAG Group, 1997]. Therefore, neutral or weakly acidic character of ESP and catalytic filter fly ashes is given by condensation products from the flue gases, i.e. mainly sulfates and chlorides. At higher temperatures these compounds are either volatilized or decomposed.

Average values of selected elements content from XRF analyses are presented in Table 2. Furthermore, high differences of elements contents were found for all ashes, therefore a variation of up to 50% could be expected. Published range [Hinton and Lane, 1991; Pekárek, 2000] is also shown in Table 2 for comparison. Trends of increase or decrease in the content of elements in studied ash fractions are depicted in Table 2 as well. The increase of Cl and S contents on fly ashes with the decrease of flue gases temperature is evident from Table 2. Chlorine and sulphur compounds with metals are volatilized at higher temperatures. This fact is confirmed by the above-mentioned changes of fly ashes acidobasic character. Similar trends corresponding to the behavior of Cl and S were also found for Cd, Cu, Pb, Sn and Zn. These results prove the fact that increasing and very high concentrations of above-mentioned elements, especially in fly ash from the catalytic filter, are mainly caused by condensation of metal chlorides and sulfates. Furthermore, decreasing amount of ash-forming elements oxides with decreasing temperature, which is evident from the data in Table 2. The highest content of these oxides was found in bottom ash, the lowest content in catalytic filter fly ash. The found behavior could be expected due to high thermal stability of ash-forming oxides.

Table 2 Contents of selected elements in ashes (average values)

| | Bottom ash | Boiler 2 nd , 3 rd pass | Boiler 4 th pass | ESP | Catalytic filter | Fly ash mixture | Trend | Published range |
|-----|------------|---|-----------------------------|--------|------------------|-----------------|-------|-----------------|
| Cl* | 14 | 57 | 130 | 200 | 220 | 160 | ↑ | 18–380 |
| S* | 18 | 70 | 85 | 68 | 140 | 75 | - | 1.4–120 |
| As | <i>BDL</i> | 90 | 180 | 160 | 280 | 150 | - | 18–960 |
| Cd | <i>BDL</i> | 160 | 650 | 780 | 2 000 | 450 | ↑ | 10–2 100 |
| Co | 170 | 140 | 90 | 60 | <i>BDL</i> | 100 | - | 1.9–300 |
| Cr | 1 200 | 910 | 1 100 | 740 | 290 | 900 | ↓ | 10–860 |
| Cu | 2 200 | 1 300 | 1 700 | 3 000 | 5 400 | 2 200 | ↑ | 16–4 100 |
| Mn | 4 100 | 2 900 | 2 800 | 1 900 | 600 | 2 400 | ↓ | 200–1 700 |
| Ni | 400 | 190 | 230 | 330 | 100 | 250 | - | 19–710 |
| Pb | <i>BDL</i> | 3 100 | 9 500 | 14 000 | 34 000 | 10 000 | ↑ | 250–27 000 |
| Sn | 500 | 950 | 2 200 | 4 200 | 8 500 | 2 800 | ↑ | 140–5 900 |

| | | | | | | | | |
|-----|-----|-------|-------|-------|-------|-------|---|----------|
| Sb | 350 | 1 100 | 2 700 | 4 400 | 6 800 | 4 200 | - | 58–3 300 |
| V | 350 | 250 | 290 | 200 | 40 | 160 | - | 4.0–150 |
| Zn* | 10 | 32 | 57 | 77 | 140 | 66 | ↑ | 0.4–100 |
| A** | 97 | 83 | 74 | 65 | 45 | 70 | | |

all in mg kg⁻¹; * in g kg⁻¹; ** in wt. %; *BDL* - below the detection limit, A - sum of ash forming elements oxides

For the practical application of solid residuals, it is very important to know the POPs contamination of ashes. Contents of polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) are shown in Table 3. In the MSWI Termizo there is relatively low contamination of fly ashes by organic pollutants. For comparison, concentrations of PCBz and PCPh in fly ashes from baghouse filters (temperature at collection point ca 150–200 °C) of old incinerators are reported to be within the range of 100–4 000 ng g⁻¹. The contents of these substances in ashes, as their concentrations in flue gases, are given by the quality of combustion process in the waste incinerator. Therefore, a high quality of combustion in the MSWI Termizo can be concluded. Furthermore, from Table 3 it is obvious that with decreasing temperature at the point of fly ashes separation, the content of organic compounds on them is increasing. There are two basic explanations of this fact. The first one and probably the more important one is that flue gases with fly ashes are passing through the “temperature window” (250–400 °C) where the formation of POPs by de novo synthetic reactions occurs. The second, which also contributes to increase of selected compounds contents in fly ashes with decreasing flue gases temperature, is the POPs condensation from the gaseous phase of flue gases.

Table 3 Contents of selected organic compounds in ashes

| ng g ⁻¹ | Bottom ash | Boiler 2 nd , 3 rd pass | Boiler 4 th pass | ESP | Catalytic filter |
|--------------------|------------|---|-----------------------------|---------|------------------|
| PCBz | <i>BDL</i> | <i>BDL</i> | <i>BDL</i> | max 100 | 250–400 |
| PCPh | <i>BDL</i> | max 50 | max 50 | max 100 | 100–250 |
| TEQ PCDD/F | max 0.1 | max 1 | max 1 | max 1 | 1–10 |

BDL - below the detection limit

The characterisation of solid residuals from the point of view of civil engineering (detailed chemical composition, morphology and pozzolanic activity, enthalpy of hydration, etc.) is presented elsewhere [Keppert et al., 2010].

PRODUCED MATERIAL

Mixture of bottom ash with acid extracted fly ashes is used for production of the material called SPRUK®. Produced material can be used as a bed construction layer for carriageways, mounds or backfills. Therefore, solid residuals from the MSWI TERMIZO were studied with respect to their composition and also properties suitable for their application in the construction industry.

Bottom ash contains β-quartz (SiO₂), anhydrite (CaSO₄), albite (Na (AlSi₃O₈)), calcite (CaCO₃), hematite (Fe₂O₃) as main crystalline components, furthermore low amounts of

portlandite ($\text{Ca}(\text{OH})_2$), hydroxyllestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$), potassium feldspar ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$) and illite ($n\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$) were also found. The acid-extracted fly ashes contain mainly $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ and in lower amounts, β -quartz. The crystallographic composition of solid residuals from different incinerators varies, e.g. fly ashes from pulverized coal power plant contain mainly aluminosilicate glass, followed by mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and quartz (SiO_2) [Moreno et al., 2005].

The successful application of the SPRUK material requires mainly its water stability, particularly low solubility and pollutants leachability. Both required features, especially very low heavy metals leachability, are provided by the fly ashes acid extraction process. Moreover, for bottom ash both unfavorable effects can not be expected to be significant. Contamination of material by the POPs is also a decisive factor for further application. Therefore, mixture of bottom ash and fly ashes was analyzed for PCDD/F content. The values of 0.12 ± 0.02 ng TEQ PCDD/F g^{-1} were found.

Table 4 shows contents of selected metals in acid-extracted fly ashes and the efficiency of acid extraction from the data obtained in the MSWI TERMIZO. Very high efficiency of acid extraction was found for Cd, Cr, Sb, and Zn. Other metals such as Cu, Ni and Pb were extracted with the efficiency of about 50%. Very low efficiency was found for As and V.

Table 4 Selected elements contents in acid extracted fly ashes

| | Fly ashes after acid extraction | Extraction efficiency (%) |
|----------------------------|---------------------------------|---------------------------|
| Al (g kg^{-1}) | 130 ± 40 | - |
| As (mg kg^{-1}) | 200 ± 50 | <10 |
| Cd (mg kg^{-1}) | 50 ± 20 | >85 |
| Co (mg kg^{-1}) | 22 ± 11 | >80 |
| Cr (mg kg^{-1}) | 180 ± 110 | >80 |
| Cu (mg kg^{-1}) | 1000 ± 270 | >55 |
| Mn (mg kg^{-1}) | 1200 ± 170 | >50 |
| Ni (mg kg^{-1}) | 110 ± 40 | >55 |
| Pb (mg kg^{-1}) | 5900 ± 2600 | >45 |
| Sb (mg kg^{-1}) | 730 ± 200 | >80 |
| Sn (mg kg^{-1}) | 1100 ± 500 | >60 |
| V (mg kg^{-1}) | 140 ± 100 | <15 |
| Zn (g kg^{-1}) | 16 ± 5 | >75 |

Table 5 Results of leachability of SPRUK (average values from year 2007)

| mg l^{-1} | Leachability of SPRUK |
|--------------------|-----------------------|
| DM | 2200 |
| DOC | 19 |
| Chlorides | 280 |
| Sulfates | 920 |

| | |
|----------------------------|------------|
| Al | 1.2 |
| Cr | 0.023 |
| Cu | 0.31 |
| Sb | 0.014 |
| V | 0.027 |
| Zn | 0.0061 |
| As, Cd, Co, Mn, Ni, Pb, Sn | <i>BDL</i> |
| | |
| pH | 10.4 |

DM - dissolved matter; DOC - dissolved organic carbon; *BDL* - below the detection limit

The most important criterion for the practical application of the SPRUK material is leachability of present pollutants. SPRUK leachability tests were performed under laboratory conditions using the standard procedures (L/S 10:1, distilled water, 24 hours). It was found that leachability of most metals was below their detection limits (see Table 5). Only Al, Cr, Cu, Sb, V, and Zn were above the detection limits; however, all these metal concentrations were below the legislative limits valid in the Czech Republic. Higher values of leachability were found only for chlorides and sulfates. Ecotoxicity of the SPRUK material was negative.

A method simulating outdoor conditions was used for more exact assessment of SPRUK behaviour and chemical stability in application. It was found that SPRUK material was not suitable for application in permanent contact with water. Under outdoor conditions (e.g., intermittent dry and rain conditions) a gradual decrease of water permeation through the material to about 20–30% of starting value at the experiment beginning was observed. Moreover, it was found that after the experiment upper layers of the SPRUK were solidified.

Outdoor tests were performed under the condition of inappropriate SPRUK usage as an upper layer of soil. However, this material is supposed to be used only as a background material, which will be covered with another layer. It is evident that under these conditions of application, contacts of the SPRUK material with water will be substantially lowered. Moreover, due to the gradual material solidification of outer layer water penetration, it would be significantly decreased. It could be expected that the SPRUK layer would flow round as a monolithic bloc in case of contacts with water.

CONCLUSIONS

Properties and character of ash fractions from municipal waste incineration plants vary very widely. Composition of incinerated waste and point of ash separation from the technological line seems to be the most important parameters affecting ash characters. All negative effects such as ash solubility, inappropriate pH, heavy metals and organic contaminants content rise with temperature decrease at the point of ash separation. Therefore, it can be concluded that bottom ash and boiler ash have a better prerequisite for application in civil engineering.

Furthermore, some waste incineration plants are equipped with ash treatment technology. In the MSWI Termizo, there is acid extraction of fly ashes by acidic technological water from the wet scrubbing system. This technology eliminates some of above-mentioned negatives,

namely fly ashes solubility and leachability of heavy metals. Mixture of acid extracted fly ash with bottom ash is used as bed construction layer for carriageways, mounds or backfills.

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