

Chemical testing of post-process ashes from municipal waste combustion

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Abstract. The results of the study presented in the paper are a part of the research project about possibility of utilization of fly ashes obtained from municipal waste combustion in production of cement binders. The main goal was to determine possibility reduction of Cl⁻ and SO₄²⁻ contents in ashes by leaching. The scope of the examination included SEM observations along with an EDS analysis of chemical composition. Preliminary results show that the major problem is the presence of heavy metals such as Cr, Ni, Cu etc.

1 Introduction

The 'Waste Management Plan of the Małopolskie Province for 2016-2022' places special emphasis on reducing and preventing generation of waste and also on its recycling. In the aspect of methods of recycling and neutralising waste, one of the courses of action mentioned is thermal processing of waste [1]. In view of the introduction in Poland, as of the beginning of 2016, of a regulation that prohibits storing high-calorific waste, as well as the EU policy aimed at reducing storage of all sorts of waste, waste incineration for energy recovery makes something of an alternative. Incineration plants produce electricity and heat delivered to municipal heat distribution networks. In the case of the Waste Thermal Treatment Plant in Krakow, the power produced is capable of illuminating the city and the heat generated provides for approx. 10% of the demand [2]. This incineration plant has a maximum capacity of 220,000 t/year, which involves continuous incineration of 14.1 tonnes per hour in two process lines. As a result of this process, the waste generated makes approx. 25% of the input products and these are bottom ash and slag, which are not hazardous waste and can be reused as building material following the process of slag treatment, as well as boiler dust, fly ash and flue gas cleaning residues. These three other types of waste are treated in stabilisation and solidification processes in order to be transformed into inert or non-hazardous waste [3]. Fly ash that is generated from combustion of coal dust is utilised in the construction industry as a concrete additive while fly ash resulting from combustion of municipal waste makes post-processing waste. In order to determine the possibility of utilisation in the construction industry it is necessary to identify its physical and chemical properties. Pursuant to PN-EN

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450-1 [4] fly ash intended for a concrete additive must comply with specific chemical requirements (Table 1) or have a technical approval certificate.

Table 1. Chemical requirements for fly ash as a concrete additive.

| Component | Requirements |
|--|--|
| Loss of ignition | Category A: $\leq 5\%$ Category B: $\leq 7\%$ Category C: $\leq 9\%$ |
| Chlorides | $\leq 0.1\%$ |
| Sulphates (VI) | $\leq 3\%$ |
| Free calcium oxide | $\leq 1.5\%*$ |
| Reactive calcium oxide | $\leq 10\%$ |
| Reactive silicon dioxide | Fly ash from co-combustion: $\geq 25\%$ |
| | Fly ash from carbon combustion: met |
| Silicon dioxide, Alumina, Iron oxide (III) | Fly ash from co-combustion: $\geq 70\%$ |
| | Fly ash from carbon combustion: met |
| Total alkali content | Fly ash from co-combustion: $\leq 5\%$ |
| | Fly ash from carbon combustion: met |
| Magnesium oxide | Fly ash from co-combustion: $\leq 4\%$ |
| | Fly ash from carbon combustion: met |
| Phosphates (V) | Fly ash from co-combustion: ≤ 100 mg/kg |
| | Fly ash from carbon combustion: met |

One of the fundamental problems hindering utilisation of the said ash is the presence of heavy metals as well as other constituents, such as chlorides and sulphates [5], which are dangerous with regard to the use and durability of concrete. This necessitate the application of various technological treatments enabling their neutralisation already at the stage of manufacturing or at the stage of application. The most popular methods include the immobilisation process or, in other words, stabilisation and solidification, which consists in transforming hazardous waste into non-hazardous to the environment by means of elution of metals and transformation of soluble sulphide and chloride compound into insoluble ones. In addition to the hydraulic binders that are characteristic for the traditional technologies, the new modern technologies also use a specially compiled set of chemicals that act in a permanent manner on the ash. An example of such a technology is the Geodur, used in Poland by the company CDF - Technologie dla środowiska s.c. [6]. Authors of the study [7] describe options of immobilising heavy metals (Cr, Zn, Cd, Mn, Pb and Cu) by means of 4 types of binders with Portland cement as well as binders containing additives of silica fly ash, ash from a fluidal boiler and ground granulated blast-furnace slag. Heavy metals were introduced in the binder as constituents of fly ash from incineration of medical waste and dust from a dedusting system of an arc furnace. It has been shown that immobilisation of these materials has been achieved at a very high level (in the range of 99.82%-99.99%); only Cr has been neutralised with a slightly lower effect (85.97%-93.33%).

In the literature there are some examples of the use of fly ashes from municipal waste combustion and researches done on them. In the article [8], the author suggests that ashes can be used in production of powder cement, ceramic tiles or concrete as a partial replacement for cement or aggregates. They can also be used in building embankments or in road building

where they could replace the sand or cement in pavements. Author confirms that by cited many publications about fly ashes from municipal waste combustion. Similar proposals for the use of ashes can be found in the article entitled "Use of Incineration MSW Ash" [9]. Also the authors of the article [10] described the possibility of using fly ashes in concrete. They focused on researches concerned information such as physical properties, durability (compressive strength) and ability to leaching. Based on the results they stated that fly ashes can be used in concrete. In turn Z. Pavlík and others in the article [11] presented the results of researches carried out on three ashes used as a filler in cement mortar, and in the conclusion they stated that, it is possible to use fly ashes in concrete, but these ashes have deteriorated the properties of concrete and first and foremost, it is necessary to focus on getting rid of the harmful elements from the ashes.

1.1 The scope and objectives of the study

The study used three types of ash from the Waste Thermal Treatment Plant in Krakow. The first type is fly ash from the flue gas cleaning system (FA 1), the second one is fly ash containing hazardous substances (FA 2), and the third one is a mixture of the other two (FA 3). All types contain heavy metals, such as mercury, lead, copper, nickel and others (Table 2). Another inconvenience is the very high content of chlorides, up to approx. 25% and of sulphates, up to several % of the mass. For this reason, an attempt was made to remove them by washing the ashes in water.

Table 2. Characteristics of the ash investigated from the incineration of municipal waste in Krakow.

| Tested parameter [mg/kg] | FA 1 | FA 2 |
|--------------------------------------|--------|--------|
| Barium | 4 | 0,34 |
| Cadmium | <0.005 | <0.005 |
| Chromium | 0.05 | 0.42 |
| Copper, mercury, molibdenium, nickel | <0.04 | <0.04 |
| Lead | 13 | <0.10 |
| Antimony | 0.029 | <0.01 |
| Selenium | 0.038 | <0.01 |
| Zinc | 4.2 | 2.7 |
| Chloride | 201382 | 18081 |
| Fluorides | 21 | 72 |
| Sulphate (VI) | 121732 | 30730 |
| Arsenic [mg/kg] | <0.01 | <0.01 |
| Dissolved organic carbon | 606 | 162 |
| Soluble substances | 498839 | 62920 |
| pH [-] | 12.1 | 12.6 |

The objective of the investigation presented in the paper was to determine the possibilities of removing soluble compounds (chlorides and sulphates) by washing ashes in water. For this purpose, an analysis was performed with regard to the contents of sulphates and chlorides in the water extracts, as well as the pH value. And the identification of the types of metal

cations in chlorides and sulphates was performed based on SEM observations of the ashes concerned together with an EDS analysis.

When considering the applicability of the ashes being tested as an alternative additive to cement binders one should bear in mind the variability of composition over time. A further problem is the presence of heavy metals for which an effective method of immobilisation must be developed, as well as a very high content of chlorides and sulphates, which are a hazard to the durability of cement-based materials.

2 The investigation and methods

2.1 Chemical analysis of chlorides and sulphates by spectrophotometry

Leaching is one of the methods of treating the ash that is generated at municipal waste incineration plants. In order to determine the possibility of removing soluble compounds (especially chlorides and sulphates) by washing, 2 water extracts were prepared for each type of ash. The first was with 1:10 ash-to-distilled water ratio (by mass); the second one was with 1:100 ratio by mass. Both were left for 24 hours. After this time, chemical analyses were performed for the first set to determine Cl^- and SO_4^{2-} contents and the pH value. The second set was filtered and the remaining residues were mixed again with distilled water at 1:10 ash-to-water ratio by mass. After 24 hours another measurement of Cl^- and SO_4^{2-} contents and the pH value was made. The chemical analyses were performed by spectrophotometry using an AQUALYTICA AL800 spectrophotometer and a CP-411 Elmetron pH-meter.

2.2 SEM observations of the ash microstructure

SEM examinations were conducted in variable vacuum on non-sputtered samples using a VPSE detector. Additionally, a chemical EDS analysis of the elemental composition was performed in selected areas. The observations along with the analysis were performed using a Zeiss EVO-MA 10 Scanning Electron Microscope equipped with a Bruker EDS XFLASH 6/30 detector. The examinations were performed for three types of ashes in the dry and free flowing condition.

3 Results and discussion

3.1 Results of determination of the content of water-soluble chlorides and sulphates and the pH value

Results of the chemical tests concerning determination of the content of water-soluble chlorides and sulphates in the ashes before and after the process of washing have been presented in Table 3.

Table 3. Results of spectrophotometric tests.

| Fly ash | Content before leaching [% mass] | | Content after leaching [% mass] | |
|---------|-------------------------------------|-------------------------------|------------------------------------|-------------------------------|
| | Cl ⁻ | SO ₄ ²⁻ | Cl ⁻ | SO ₄ ²⁻ |
| FA 1 | 27 | 0.66 | 0.2 | 0.12 |
| FA 2 | 21 | 0.71 | 0.26 | 0.12 |
| FA 3 | 6 | 1.16 | 0.05 | 0.35 |

The results that were obtained indicate a possibility of removing considerable amounts of Cl⁻ and SO₄²⁻ from the test ashes by washing in water. Washing enables removing over 90% of chlorides present in the fly ashes examined. Their pH value both before and after washing is strongly alkaline and is in the ranges of 11.8÷12.3 and 11.1÷11.6 respectively.

3.2 Results of SEM examinations with an EDS analysis

Results of SEM observations along with mapping images of selected elements (O, Ca, Cl, Na, K, S, Si, Al and Ba) have been shown in Figures 1÷3.

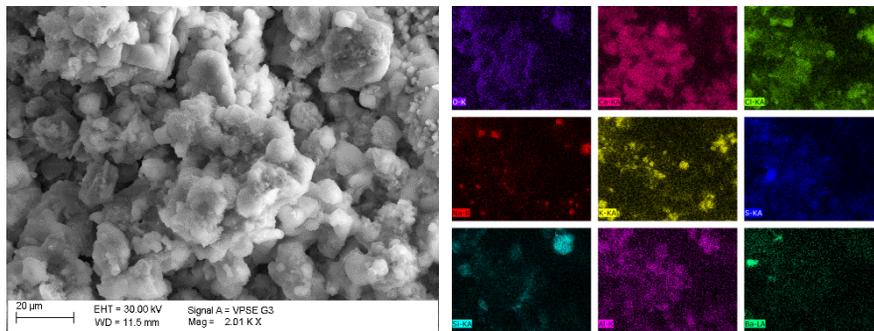


Fig. 1. SEM image of fly ash 1 with mapping of chosen elements.

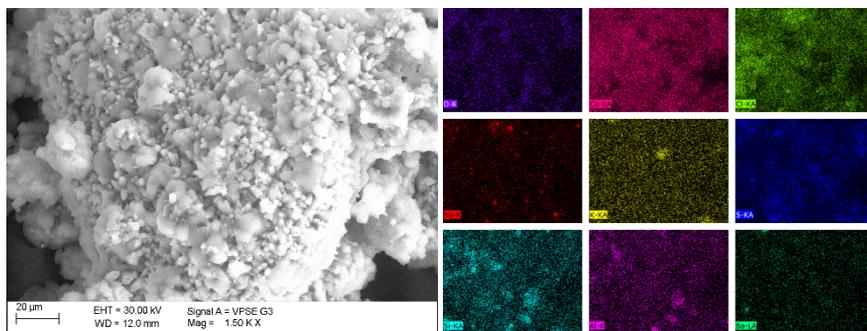


Fig. 2. SEM image of fly ash 2 with mapping of chosen elements.

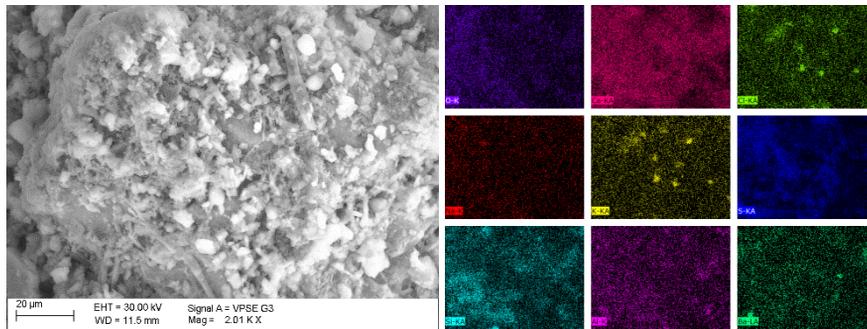


Fig. 3. SEM image of fly ash 3 with mapping of chosen elements.

In the microstructural examinations special focus was placed on the crystalline form of chlorides and sulphates. These are predominantly KCl crystals, more seldom NaCl, which take the form of fine and thick crystals. Sulphates occur most probably in the form of gypsum but, due to the high content of calcium compounds, this is difficult to determine based on EDS analysis alone.

4 Conclusion

The results presented in the paper form a part of a preliminary investigation the purpose of which was to determine the possibilities of utilising the ash in question in the construction industry. Due to a very high content of chlorides and sulphates, the examination was commenced with an attempt at removing these compounds using the method of washing in water. The results obtained give reasons to think that this is an effective method that enables reduction of Cl^- and SO_4^{2-} contents below a few % of the mass. However, it is necessary to conduct supplementary investigation concerning all the substances that are simultaneously washed out from the ash.

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