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EDITOR

Snežana Šerbula

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PREFACE

The rapid development of industry and technology, the increased demand for using fossil fuels and exploitation of primary raw materials call into question sustainability of progress in today's society. Environmental research and ecological truth are the main subjects of the 26th International Conference Ecological Truth & Environmental Research 2018 (EcoTER'18), which will be held at Bor Lake, Serbia, 12-15 June 2018. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

The EcoTER'18 is organized by the Technical faculty in Bor, the University of Belgrade and co-organized by the Faculty of Technology, University of Banja Luka, the Faculty of Metallurgy and Technology, Podgorica, the Faculty of Metallurgy, Sisak and the Society of Young Researchers, Bor.

The primary goal of EcoTER'18 is to bring together academics, researchers, and industry engineers to exchange their experiences, expertise and ideas, and also to consider possibilities for collaborative research.

This year's conference is dedicated to the memory of Professor Zoran Marković, who organized the Conference for many years and who was one of our most loyal and active Committee members.

These proceedings include 77 papers from authors coming from universities, research institutes and industries in 13 countries: Argentina, Poland, Republic of Belarus, Turkey, France, Italia, Romania, Bulgaria, Croatia, Bosnia and Herzegovina, Macedonia, Montenegro, and Serbia.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged. The support of the sponsors and their willingness and ability to cooperate has been of great importance for the success of EcoTER'18. The Organizing Committee would like to extend their appreciation and gratitude to all the sponsors and friends of the Conference for their donations and support.

We would like to thank all the authors who have contributed to these proceedings, and also to the members of the scientific and organizing committees, reviewer, speakers, chairpersons and all the Conference participants for their support to EcoTER'18. Sincere thanks to all the people who have contributed to the successful organization of EcoTER'18.

*On behalf of the 26th EcoTER Organizing Committee,
Snežana Šerbula, PhD Full Professor*

CHARACTERISTICS OF FLY ASHES, THEIR POTENTIAL USES AND DAMAGED CONDITIONS OF LANDFILL DEPOSITS

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Abstract

Diverse industries produce fly ashes as thermal power plants, waste incinerators, and some recycling processes. Though some of these products can be raw materials for diverse applications, their composition can be hazardous due to their content in heavy metals. In addition, mixing fly ashes with the products of neutralization of fumes complicates the products. Then many fly ashes are landfilled in a Portland-cement matrix. However, most of the actual knowledge about their ageing derives from models the validity of which has been established only on the short term, using small sized proofs, at room conditions while matter transfers and reactions are strongly affected by temperatures reaching 80 °C for many years. Ageing leads to a mobility of chlorides, sulphates and lead, alteration of textural properties with formation of microcracks, formation of neo-formed minerals as silicate-hydrates (katoite and hibschite, CSH), carbonates, tobermorite, hydrogarnets zeolites,...) that can contribute to bear Pb, Zn, Cr, Cu, in addition to inherited phases (metallic alloys, spinels, glasses, refractory oxides, titanates, phosphates,...). The alkaline hydrolysis of aluminium in saline media decreases the pH and promotes the precipitation of lead species trapped in a hydrocalumite or ettringite matrix.

Keywords: Fly ashes, Cement based matrix, Long-term evolution

INTRODUCTION

Municipal waste treatment, thermal power plants and some elimination-beneficiation devices devoted to decayed composite materials produce fly ashes. The incineration of municipal waste is currently used to reduce volume, recover energy, reuse materials and control residues. The so-called Municipal Solid Waste Incinerator (MSWI) fly ashes also contain added materials as neutralizing products of fumes, and then high content of inorganic mobile components as chlorides, sulphates and heavy metals. Due to their fineness and their high inorganic pollutants potential, the MSWI are hazardous materials that cannot be valorized nor recycled, in Western Europe, their production reaches about $1.2 \cdot 10^6$ tons/year, what generates environment problems; solidification/stabilization (S/S) industrial methods have been developed to solve them. The S/S process based on hydraulic binders is often used to stabilize MSWI fly ashes [1]. In this procedure, the solids are usually mixed with cement and water or with bitumen, with or without other additives (lime, pozzolanic reagents...) and, finally, mainly disposed in landfills, producing huge monoliths also called monofills [2].

Three classes of such landfills exist, the class 1 is devoted to hazardous materials. The question of potential utilizations of MSWI fly ashes (fillers in concretes [3], material for ceramics...) is also explored and need to know their long-term behavior.

MSWI fly ashes S/S involving hydraulic binders has been used for years, however, its long-term durability remains an open question. Most of the knowledge about the element mobility depends on models the validity of which has been established on the short term, using small sized proofs, at room conditions [4,5]. A difficulty remains to build mobility models for monofills submitted to weathering, since the porosity and the nature of phases evolve over time. This study aims at clarifying the mineralogical status of several heavy metals, mainly Pb, Zn and Cr, and anions, as SO_4^{2-} and Cl^- , to predict their long-term behavior. Others elements as Cd, As and Hg, also impact the environment, they volatilize during combustion, condense on the finest particles and occur at low local concentrations [6], approaching their speciation needs a high-resolution determination that will not be considered here.

Two disposal sites were considered. One, with MSWI fly ashes stabilized with Portland cement without any previous treatment was ten years old (site A); the other, with MSWI fly ashes stabilized with cement after a partial leaching and precipitation of soluble heavy metals using Na_2S , was five years old (site B). In both monofills, the S/S MSWI fly ashes have not been covered so that they have been submitted to atmospheric weathering. Aged samples were also compared with fresh materials and small test-bars.

MATERIALS AND METHODS

Raw residues were collected from the filters and gas scrubbers of the two incineration plants. For the residues corresponding to the site A, the filter fly ashes and the gas scrubber salts were collected separately, while the sample of the site B is a mixture of fly ashes and salts. Sampling of the site B was performed using a hammer-drill, since core-drilling was impossible, due to the poor cohesion of the materials. The monoliths were sampled from top to bottom. Small test-bars (A) realized by mixing the raw MSWI residues with Portland cement and water were also analyzed.

The quantities of samples taken from site B with the drilling-machine were not sufficient, because of drilling problems. Thus, the monolith was trenched, and the trench sampled. During excavating, an important release of water vapor was noticed, which indicates a high temperature inside the monolith. Furthermore fresh blocs of solidified/stabilized MSWI fly ashes obtained in the plant B have also been analyzed.

Characterization analyses are detailed in Antenucci *et al.*, [7] and summarized in Yvon *et al.*, [8], they concern chemical bulk analyses, compliance tests, permeability, mineralogy, petrographic analysis and micro-analysis by SEM or TEM.

RESULTS AND DISCUSSION

According to chemical analysis and compliance leaching tests, the bulk concentrations of Pb and Zn are rather high, high leached amounts of Pb and Zn are measured from the raw materials. For the solidified materials, the highest leached amount is displayed by Pb, whereas Zn is systematically leached below the European regulation limit. In some cases, leached amounts of Cr exceed the accepted limit. The SO_4^{2-} leached quantities are often above the European limit whereas the Cl^- leached concentrations are systematically higher.

Compared with classical concretes, the solidified MSWI fly ashes show a high permeability. The water drain-off through test-bars ranges between 4000 and 6500 cm³ instead of 11 cm³ in case of a convenient concrete. Such elevated values result of the low cohesion of the material. Despite the lack of porosity measurement, this high permeability depicts a risk of mobilization of toxic elements by weathering.

The petrographic analysis exhibits common texture and composition of the samples. Networks of micro-cracks, related to hydration-dehydration cycles and/or to shrinkage, and reactions with dissolution at very high pH and/or replacement by portlandite, sulphates, titanates or hydrocalumite are observed. No carbonation discrepancy was observed between the various aged samples at the scale of polarizing microscope.

Based on XRD the materials A and B, contain the same mineral phases. The salts A are mainly enriched in CaCl₂·Ca(OH)₂·H₂O, portlandite and calcite, while the fly ashes contain calcite, halite, sylvite, fluorite, anhydrite, quartz, hematite, magnetite and pyrite. Portlandite, calcite, CaCl₂·Ca(OH)₂·H₂O, sylvite and halite are present in the A samples. Only calcite remains as a major mineral in B, but in the fresh S/S MSWI B, portlandite and calcite are the main inherited phases. Ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) and hydrocalumite (Ca₂Al(OH)₆(Cl,OH)·3H₂O) are formed by weathering in all the S/S MSWI, and katoite (Ca₃Al₂(SiO₄)_{3-x}(OH)_{4x}), gonnardite, (Na₂CaAl₄Si₆O₂₀·7H₂O) and tobermorite (Ca₅Si₆(O,OH)₁₈·5H₂O) in B. No mineralogical discrepancy has been observed between cored and trenched samples. Both the test-bars and fresh samples are free of katoite, gonnardite and tobermorite. Since the mineralogical analysis does not reveal any vertical gradient concerning calcite, the carbonation has minor effects.

Neither the raw MSWI residues, nor the S/S MSWI fly ashes contain any pollutant bearing minerals, indicating that those phases are either absent, amorphous or under the detection limits. Thus TEM and SEM were involved to complete the XRD characterization. The back-scattered electron imaging shows that generally these particles are finer than 10 μm, SEM-EDS and TEM-EDS analyses indicate the presence of metals in different inherited or neo-formed minerals. The pollutant bearing minerals in the two sites are rather analogues, except sulphides that are more present in B due to the sulphidation pre-treatment.

Among the inherited phases: the stable phases are glasses containing zinc, lead and chromium, metallic alloys, spinels, oxides, hydroxides, phosphates containing lead and zinc, mainly those of the apatite group, zinc titanium oxides and zinc silicates. The inherited unstable phases are amphoteric metals, calcium chromates, hydroxy-chlorides and chlorides more abundant in the A samples.

Except for hydrogarnets, katoite or hibschite, that contains some Zn, the other major neo-formed phases, hydrocalumite and ettringite are free of transitional cations. Considering the minor neo-formed phases, actually ordered silicates hydrates (afwillite) and hydrocalcite group minerals, only the later contains some Zn. The limited cationic substitution observed in these minerals is in contrast with the data reported in the literature [9-13].

Some minor neoformed phases are stable as diverse Ca/Zn titanates, zinc phosphate (hopeite), Zn and Cr in barium sulphate (hachemite), mixed Pb/Cu/Hg sulphides, and mixed Pb/Cu hydroxysulphates. Some others are unstable as lead chlorides and hydroxychlorides, lead hydroxide, resulting from the hydrolysis of aluminium followed by the precipitation of aluminium hydroxide, hydrocalumite, and hydrocerusite.

The incorporation of Pb and Zn in the CSH compounds corroborates the data reported in the literature [13]. However, samples B show that Pb occurs mainly as PbS that precipitates during the pre-treatment.

The petrographic approach reveals a network of connected micro-cracks that explains the high permeability of solidified materials, promote fluids circulation, facilitating the leaching and the chemical reactions, then the removal of pollutants.

The presence of hydrocalumite and ettringite in the solidified samples explains the behavior of Cl^- and SO_4^{2-} under leaching. Hydrocalumite is a soluble mineral at any pH, the Cl^- leached amounts are not drastically lowered by the S/S process and, then, the solidified MSWI fly ashes behaves as hazardous material with regard to Cl^- . The ettringite solubility decreases when pH increases [14], the SO_4^{2-} leached amounts are significantly reduced compared to the starting raw material, but are often above the accepted European limit. Thus, ettringite cannot ensure an ideal immobilization of SO_4^{2-} .

The temperature measured *in situ* when sampling the site B was close to 70°C. In monofills, the temperature probably reaches 100°C, what generates a convection of fluids. This phenomenon can arise from slow or differed exothermic reactions without fast evacuation of energy. The temperature and the circulation of fluids promote the crystallization of ordered silicate-hydrates, namely zeolites, hydrogarnets and tobermorite. Natural Si-rich hydrothermal solutions are known to promote the crystallization of silicate-hydrates in fractures and cavities where katoite, ettringite, tobermorite, afwillite, chabazite, etc., crystallize [15].

Temperature indications are also supported by data available in the literature. Gonnardite, is synthesized between 100 and 120°C from coal fly ashes [16], and tobermorite can be stable between 80 and 140°C [17]. Usually the hydration of concrete minerals generates disordered hydrates, named CSH, that trap one significant part of soluble zinc and lead, and bring a low permeability to the whole in such a way that soluble lead and zinc salts can crystallize in vacuoles [18]. In the present cases, the ordered hydrates are almost free of metallic pollutants, lead is concentrated in leachable phases and micro-cracks increase the permeability.

Despite the fact that no *in situ* temperatures have been measured for the site A, the presence of hydrocalumite, as a major phase, as well as hydrotalcite and Zn-hydrogarnet, as minor phase, suggest temperatures close to those indicated for the site B. Several layered double hydroxides (LDHs), [12-19], have been synthesized in hydrothermal conditions between 65 and 110°C [20,21]. The test-bars reveal drastically less heavy metal-bearing mineral species. By analogy with the above considerations on silicate-hydrates major phases, such a result shows that the differentiation of minor species also requires a prolonged exposure to high temperature. This information is particularly indicative of the limit of reliability of models established at laboratory scale, from which the long-term behavior of solidified/stabilized MSWI fly ashes in cement matrix are deduced.

Pb, Zn and Cr are distributed between different phases: inherited stable phases (metallic alloys, spinels, glasses, refractory oxides, titanates, phosphates...), inherited or neo-formed unstable phases (amphoteric metals, hydroxides, carbonates, chlorides, chromates...). The neo-formed Pb-chloride and oxy-chlorides identified in solidified/stabilized materials are linked to the hydrolysis of aluminium, which leads to the following systematic sequence: aluminium (core zone)/aluminium hydroxide (intermediate zone)/hydrocalumite (external zone). Pb-minerals, smaller than 1 μm , crystallize inside the hydrocalumite zone [7,8].

No cationic substitution occurs in ordered silicate-hydrates compounds, except for katoite where some Zn^{2+} substitutes for Ca^{2+} . In addition, the heavy metals-bearing minor minerals display cationic substitutions involving Zn and/or Cr, but do not show substitutions involving Pb. The fact that ordered silicate-hydrates are essentially free of Zn and Cr ions indicates that a significant part of these cations are fixed irreversibly in the starting materials, through the

formation of spinels, glasses, refractory oxides, etc., at high temperature, their high stability explains the low leached amounts of Zn and Cr. The fact that some samples display Cr leached concentrations higher than the European acceptable limit is due to the soluble chromate minerals. The question of Pb needs a more extended discussion. It is well known that Pb^{2+} often substitutes for Ca^{2+} , as in phosphates of the apatite group [22,23] or arsenates, such as tsumcorite, $(\text{Ca}, \text{Pb})(\text{Zn}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Mn}^{3+}, \text{Co})_2 (\text{AsO}_4)_2 \cdot (\text{H}_2\text{O}, \text{OH})_2$ [24]. To explain the unexpected observed results, the electronic configuration of Pb must be considered [25]. The one-sided arrangement of bonds to anions is typical of the stereochemically active $6s^2$ lone-pair behavior for Pb^{2+} , which leads to quite irregular Pb polyhedra. In particular, this situation can be observed in various Pb-oxy-chlorides, for instance those displaying the common thorikosite-type structure, $\text{Pb}_3\text{SbO}_3(\text{OH})\text{Cl}_2$, which includes, among others, symesite, $\text{Pb}_{10}(\text{SO}_4)\text{O}_7\text{Cl}_4(\text{H}_2\text{O})$ [25], pinalite, $\text{Pb}_3(\text{WO}_5)\text{Cl}_2$, and blixite [26], where the active $6s^2$ lone-pair effects manifests by drastically decreasing the average Pb-O bond length and increasing the average Pb-Cl bond length in the Pb-sites [25]. Available crystallographic data for katoite [27], ettringite [28] and hydrocalumite [29] indicate regular Ca-sites, suggesting an incompatibility with the geometry required by the electronic configuration of Pb^{2+} . Thus, the crystallochemistry constrains combined with the high activity of Cl^- and the basic pH in the cement-based solidification/stabilization, promotes the crystallization of Pb-species, favouring the precipitation of unstable Pb-minerals. This situation is responsible for the high level of leached Pb in A samples. In the samples B, given the pretreatment of raw materials the activities of Cl^- and S^{2-} are reduced and Pb can be partially incorporated in more stable sulphide minerals such as PbS. Furthermore, the Pb-hydroxides, Pb-chlorides and oxy-chlorides, the most abundant Pb-bearing phases, are trapped inside hydrocalumite zones that are more micro-cracked in A than in B samples [7]. As a consequence, in the B S/S MSWI fly ashes, the unstable Pb-minerals are temporary screened by the hydrocalumite zones: a situation that promotes a time-lag Pb leaching off.

CONCLUSION

The compliance leaching tests cannot predict, alone, the long-term evolution of pollutants in MSWI fly ashes solidified/stabilized in cement matrix. Monofills of solidified/stabilized MSWI fly ashes using hydraulic binders are affected by a prolonged exposure to temperature close to 100°C that governs the evolution of major mineral phases and the differentiation of metal bearing minor ones. Disordered hydrates form at low temperature, they trap one part of heavy metals and generate a low permeability barrier. At high temperature hydrates are ordered, do not accept heavy metals in their lattice and generate a highly porous barrier. The zinc and in part chromium bearing phases are stable, whereas mineral species containing lead, Cl^- and SO_4^{2-} are unstable, despite the maturation. Finally, the solidification/stabilization of MSWI fly ashes through hydraulic binders is rather not the right solution with regard to SO_4^{2-} , Cl^- and Pb. At present time, given their hazardous character due to the instability of lead and anions-bearing phases, the S/S MSWI fly ashes must be managed in landfills devoted to hazardous wastes.

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