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LEACHING BEHAVIOUR OF ESTONIAN OIL SHALE ASH-BASED CONSTRUCTION MORTARS

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Abstract. *To estimate the environmental properties of oil shale ash-based mortars the leaching of harmful components was studied. The leachates were highly alkaline. The predominant ions were* Ca^{2+}, K^+, Na^+, SO_4^{2-}. *The leachable content of soluble components in PF ash mortars was higher in comparison with that in CFB ash mortars. Results indicated that over curing time the fraction of readily soluble inorganic components decreased and the mobility of potentially hazardous Cd and Zn did not increase. Addition of bypass dust could affect the content of leachable ions. Results give new knowledge about the environmental properties of oil shale ash-based materials, including backfilling composites for underground mining technology.*

Keywords: *oil shale ash, bypass dust, mortar, leaching, Cd, Zn.*

1. Introduction

Oil shale (OS), a local low-calorific fuel, is an important source for power generation in Estonia. The main by-product of OS processing is oil shale ash (OSA). Due to its high mineral content the combustion of OS generates a huge amount of ash. The mechanisms of formation of OSA have been described in the literature [1–4]. The physical and chemical properties of ash, in general, are quite variable, as they are influenced by the source and particle size of OS, and type of its burning process [3, 4]. Narva Power

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Plants (Narva PPs) implements two different OS combustion technologies: pulverized-fired (PF) and, within the last decade, circulating fluidized bed (CFB) combustion [1, 2, 5]. The high-temperature combustion process in PF boilers (1350–1450 ^{o}C) ensures a major decomposition of carbonate mineral phases (dolomite, calcite) and melting of clay minerals that form a source of reactive silica as well as aluminium, thus controlling the formation of secondary Ca-silicate and Ca-Al-silicate phases. The firing temperature in CFB boilers (about 850 °C) allows thermal decomposition of dolomite, but only partial decomposition of calcite [4]. Also, the clay mineral phases are preserved. CFB ashes contain a higher share of residual mineral phases in comparison with PF ashes. A specific characteristic of CFB ashes is also their higher concentration of sulphur [4].

Kuusik et al. [3] and Bitjukova et al. [4] demonstrated that all OSA fractions are dominated by the presence of CaO_{total}, whose proportion varies from 26 to 55% in PF ash and from 26 to 49 % in CFB ash. As reported [2, 3, 6, 7], OSA is rich in free lime (CaO_{free}), anhydrite ($CaSO_4$), secondary Ca(Mg)-silicate minerals and, especially in PF ashes, an amorphous Al-Si glass phase.

According to Kuusik et al. [7], variations in the mineral composition of ash fractions are related to those in the lime, the proportion of which varies from about 1.6% in CFB ash to a maximum of 24.6% in PF ash. Due to the significant difference (1.5–1.8-fold) in their combustion temperatures, the difference in amorphous-glassy phase content between PF and CFB ashes is also evident. In PF ash fractions the content of the amorphous phase varies from 38% in cyclone ash to 28%, 23% and 1% in ashes from the first, second and third fields in the electrostatic precipitator, respectively. In CFB ashes the content of the amorphous phase is about 10–15% [6, 7].

OSA has been classified as a hazardous waste because of its high alkalinity (Material Safety Data Sheet for Burnt Oil Shale according to EC regulations No 1907/2006 and EU No 453/2010). The elemental composition of OSA comprises trace elements and potentially toxic heavy metals, including Cd and Zn [8–11]. Studies [5, 8] have demonstrated enrichment of Co, Cu, Hg, Ni and Sb as well as Cd, Pb and Zn in PF ashes from electrostatic precipitators and cyclones relative to raw OS. The concentration of Cd and Zn in the fine PF ash fraction (< 6 μm) collected from the Eesti Power Plant of Narva PPs was 3.5 ppm and 380 ppm, respectively [5]. The concentration of elements in the fine fraction of OSA from the Balti Power Plant, Narva PPs, was found to be 1.3 and 219 ppm for Cd and Zn, respectively.

It is known that when fly ash is in contact with water, dissolution of the solid phase occurs, with changes in pH and the release of potentially harmful components [12–16]. The principal processes affecting the leaching process are dissolution of primary solids as well as sorption and hydrolysis reactions, etc. [12–16].

A massive amount of OSA produced is wet deposited in ash fields [6, 7, 17] and causes a significant environmental problem due to the presence of harmful components and the high alkalinity of leachates [17–21]. At the same time, a number of studies have demonstrated that industrial by-products such as combustion ash can be used as raw material in the construction industry [20, 22–29]. Similarly to the use of coal fly ash, a promising area could be using OSA for the production of concrete [3, 25, 28, 29]. On the other hand, there is a growing interest in the environmental impact of cement-based materials, especially of materials containing industrial by-products [20, 30–33]. The main aspect of the ecological risk associated with reuse of mineral waste is the leaching of inorganic contaminants when the materials are in contact with water [20, 24, 33, 34]. A composite material is a combination of two or more materials (in certain proportions) whose characteristics differ from those of its individual components [35, 36]. In this context there is a lack of data concerning the environmental properties of construction materials (including backfilling composites for mining industry) based on OSA or OSA with added cement production residue bypass dust (BD).

The aim of the current study was to generate new knowledge about the leaching behaviour of mortars containing different types of OSA or OSA and BD in contact with water. The specific objectives were:

- to assess the leaching of inorganic soluble components, including hazardous Zn and Cd, from PF ash or CFB ash-based mortars after a 7-, 28- or 91-day curing period as compared to the initial OSA samples;
- to assess the effect of BD addition on the leaching behaviour of OSA-based mortars after a curing period of 7, 28 or 91 days.

2. Materials and methods

2.1. Materials

Three PF ash samples, including ash from the 1st to 3rd fields of electrostatic precipitators (ESPs) (1A EF1-3), ash from the 1st field of the electrostatic precipitator (1A EF1) and cyclone ash (1A CA), as well as two CFB ash samples from the 1st field of the ESP (8A EF1) and an ash mixture ($8A_{mix}$) were used in this study. Ash samples were collected from the Eesti Power Plant. BD is a waste by-product that is generated in the production of cement. A BD sample was obtained from AS Kunda Nordic Cement, Estonia.

2.2. Apparatus

The chemical composition of the ash and BD samples was determined by XRF analysis on a Rigaku Primus II using a ZSX Version 3.44. Carbon content was determined on an ELTRA CS 580 Carbon Sulphur Determinator. The mineral composition of the crystalline phases was determined by XRD analysis on a Bruker D8 Advanced diffractometer. Specific surface area (SSA) was estimated using the Brunauer-Emmet-Teller (BET) method on a KELVIN 1042 sorptometer (Costech Microanalytical SC, Estonia). An LA-950V2 laser scattering particle size distribution analyser (Horiba) was used to measure particle size.

2.3. Preparation of mortars

Mortars containing ash alone (100% ash, wt.) or appropriate amounts of ash (99%, 95% or 90% wt.) and BD (1%, 5% or 10% wt.) with dimensions of 40 × 40 × 160 mm were made by mixing the binder with sand (EVS-EN 196-1) at a 1:3 weight ratio and with water to equal consistency. The mortars were hardened in moulds for 48 ± 2 hours and after that for five days at 20 ± 2 ºC and a relative humidity (RH) of 65 ± 5%. Then the specimens were further hardened at 20 ± 2 ºC and 95 ± 5% RH until testing. After 7, 28 and 91 days of curing the mortars were prepared for testing of their leaching properties by crushing and sieving them through a 1 mm mesh.

2.4. Leaching test

A batch leaching test according to the European Standard EN 12457-2(2002) [37] was carried out. For the environmental characterization of combustion by-products the so-called shake test is used, which is based on waste materials [10, 12, 14, 16, 17] according to the Council Decision 2003/33/EC. The test provides information on the leaching of soluble constituents upon contact with water under the experimental conditions. The test was performed with two subsequent extraction cycles of the same portion of material with a fresh amount of water. The water extracts (leachates) were then used for further chemical analysis.

The following procedure was applied: each sample (60 g) was leached with deionized water (Milli Q) (liquid/solid ratio 10 L/kg) during 24 hours at room temperature (20 ^{o}C). At the end of extraction the suspension was filtered through a 0.45 μm filter (HIMFIL, Estonia). The solids were quantitatively returned to the flask, a fresh portion of deionized water was added and the leaching/filtration procedure was repeated. Blank tests without sample but applying the same procedure were carried out in parallel for each set of analyses. Two replicate samples were used and the test results were averaged.

2.5. Chemical analysis of leachates

The parameters of the leachates determined were pH, conductivity (EC), and the concentrations of ions Ca^{2+}, K^{+}, Na^{+}, Mg^{2+}, SO_4^{2-}, Cd^{2+} and Zn^{2+}.

The pH (H_2O) and EC (μS/cm) were measured using a BENCH PC 510 pH/Conductivity Meter (Eutech Instruments Pte Ltd, Singapore/Oakland Instruments, Vernon Hills, IL, USA).

The concentration of SO_4^{2-} was analysed using a SpectroDirect Lovibond No 400228 spectrophotometer. The concentrations of Ca^{2+}, K^+, Mg^{2+}, Na^+, Cd^{2+} and Zn^{2+} were determined with a SpectrAA 55B Flame Atomic Absorption Spectrometer.

3. Results and discussion

3.1. Main characteristics of OSA and BD

The OSA fractions used in the current study (Table 1) were similar in chemical and phase composition as well as physical characteristics to those employed in previous works [3, 4]. The composition and characteristics of ashes varied considerably depending on the separation point and the oil shale burning technology.

XRD analysis (Table 1) indicated that compared to the PF OSA fractions (1A EF1, 1A CA), the CFB OSA ($8A_{mix}$, 8A EF1) contained more calcite ($CaCO_3$) and less free lime (CaO_{free}). Due to the relatively high amorphous phase content in PF OSA [38] the results of the qXRD analysis do not agree with those of standard chemical analysis of CaO and $CaCO_3$ contents (Table 1). In CFB OSA samples, silica compounds were mainly represented by quartz (SiO_2) and orthoclase type K-feldspar ($KAlSiO_3$), while the PF OSA samples contained noticeably more secondary silicates – belite (Ca_2SiO_4) and merwinite ($Ca_3Mg(SiO_4)_2$). BET measurements (Table 1) revealed a significant difference in physical structure between CFB and PF ashes. $8A_{mix}$ and 8A EF1 ashes possessed the surface area of up to 5.87 m^2/g, while that of 1A EF1-3 and 1A EF1 ranged between 0.42 and 1.03 m^2/g, respectively.

The chemical composition of bypass dust (BD) was characterized by a high content of CaO, SiO_2 and K_2O (Table 1). BD consisted predominantly of calcite, belite and K-feldspar. The specific surface area value was 3.00 m^2/g and d_{mean} was 41.43 µm.

3.2. Leaching of OSA and BD

A leaching test was carried out in order to estimate the leaching characteristics of the initial OSA and BD samples. The results are summarized in Table 2, which represent the mean ± SD of two parallel experiments.

All leachates were highly alkaline (ca 13) (Table 2). The mean pH and EC of leachates from the first extraction cycle were higher than those of the second leachates. Therefore, a very significant portion of the readily soluble inorganic components was already leached during the first extraction cycle.

The data indicated that the leaching behaviour of the studied OSA samples depended on the combustion technology used.

Table 1. Main characteristics of oil shale ash fractions [7] and a bypass dust sample

Content, wt%	BD	1A EF1-3	1A EF1	1A CA	$8A_{mix}$	8A EF1
Chemical composition						
CaO	38.9	nd	37.9	49.6	39.4	30.2
MgO	1.3	nd	2.4	3.3	3.9	3.4
K_2O	8.8	nd	5.7	2.0	2.4	4.6
Al_2O_3	3.9	nd	7.8	4.8	5.9	10.3
SiO_2	14.0	nd	29.8	21.1	20.1	35.1
Fe_2O_3	1.9	nd	3.8	4.2	3.5	4.7
SO_3	7.4	nd	7.8	4.7	4.6	4.3
CO_2	17.8	1.3	1.8	1.2	16.6	4.2
Cl	2.1	nd	0.5	0.2	0.2	0.3
P_2O_5	0.3	nd	0.2	0.1	0.1	0.2
N_2O	0.3	nd	0.1	0.04	0.07	0.13
TiO_2	0.2	nd	0.5	0.3	0.4	0.6
Cr_2O_3	0	nd	0.02	0	0.01	0.02
MnO	0.08	nd	0.06	0.07	0.07	0.06
NiO	0.005	nd	0.008	0.006	0.007	0.008
Σ	96.895	–	98.529	91.616	97.2	98.2
Phase composition						
SiO_2	4.8	8.6	7.8	4.4	19.9	20.2
$KAlSiO_3$	11.7	6.2[a]	8.1	3.9	16.1	15.4
$CaCO_3$	42.0	6.2	7.3	3.3	10.7	10.5
CaO	3.6	7.8	20.2	28.3	10.7	12.6
$CaSO_4$	0.1	24.6	15.3	8.6	9.6	9.4
MgO	1.1	3.4	4.7	5.1	2.6	2.5
$CaSiO_3$	3.4	2.4	2.3	3.7	1.1	0.9
Ca_2SiO_4	14.4	18.3	16.8	24.0	8.2	7.4
Ca_3SiO_5	5.1	nd	3.8	0	1.2	0.9
$Ca_3Mg(SiO_4)_2$	1.2	1.5	1.0	6.3	0.7	0.8
$(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	0.7	nd	2.4	8.2	1.9	1.7
$4CaO*Al_2O_3*Fe_2O_3$	0	2.2	1.6	2.4	0.7	0.4
Fe_2O_3	0	3.3	1.7	1.3	2.9	3.0
$Ca_{11}(SiO_4)_4O_2S$	0	nd	1.5	0	1.9	1.6
$2CaO*Fe_2O_3$	0	nd	2.5	0	1.2	1.3
KCl	3.7	2.1	0	0	0	0
$KAl_2(Si_3AlO_{10})\cdot(OH)_2$	0	nd	0	0	9.0	9.6
K_2SO_4	8.1	2.3	0	0	0	0
Σ	99.9	91.4[b]	97.0	99.5	98.4	98.2
Physical characteristics						
BET SSA, m^2/g	3.00	1.03	0.87	0.42	3.88	5.87
d_{mean}, μm	41.43	9.09	18.19	61.73	nd	35.36

nd – not determined

[a] K – feldspar, $KAlSi_3O_8$

[b] including akermanite (CaMgSi2O7) 0.6%, portlandite (Ca(OH)2) 10.5%

Abbreviations used: BD – bypass dust; 1A EF1-3 – pulverized-fired (PF) ash from the 1st to 3rd fields of electrostatic precipitators; 1A EF1 – PF ash from the 1st field of the electrostatic precipitator; 1A CA – PF ash from cyclone; $8A_{mix}$ – circulating fluidized bed (CFB) ash mixture; 8A EF1 – CFB ash from the 1st field of the electrostatic precipitator.

Table 2. pH, conductivity (EC, µS/cm) and leachable content of major ions (mg/kg) in oil shale ash and bypass dust samples

Parameter	OSA					BD
	1A EF1-3	1A EF1	1A CA	$8A_{mix}$	8A EF1	
First leachate						
pH	13.1±0.02	13.1±0.02	13.0±0.03	13.3±0.03	13.1±0.03	13.3±0.03
EC	14440±29	13540±27	11180±22	10880±22	11520±23	26800±54
Ca^{2+}	12900±26	13759±28	7920±16	9290±19	9859±20	8700±17
K^{+}	5174±10	3069±6	72±0.1	578±1	1015±2	14575±29
Na^{+}	83.0±0.2	51.0±0.1	4.0±0.1	17.0±0.1	28.0±0.1	691.0±1.4
Mg^{2+}	<0.1	n.d.	n.d.	<0.2	<0.1	n.d.
SO_4^{2-}	18040±36	15350±31	4500±9	11980±24	5700±11	34700±69
Second leachate						
pH	13.0±0.02	13.1±0.02	13.0±0.02	13.0±0.03	13.1±0.02	12.96±0.03
EC	10800±22	10900±22	10120±20	8540±17	8200±16	8240±17
Ca^{2+}	12238±24	11561±23	8780±18	1337±3	6383±13	1070±2
K^{+}	453±1	262±1	572±1	329±1	582±1	1229±2
Na^{+}	14.0±0.1	10.0±0.1	12.0±0.1	18.0±0.1	28.0±0.1	822.0±1.6
Mg^{2+}	<0.1	n.d.	n.d.	< 0.2	n.d.	n.d.
SO_4^{2-}	12050±24	10200±20	9910±19	5160±10	–	5900±12

n.d. – not determined
– no data
Abbreviations used: OSA – oil shale ash; BD – bypass dust; 1A EF1-3 – pulverized-fired (PF) ash from the 1st to 3rd fields of electrostatic precipitators; 1A EF1 – PF ash from the 1st field of the electrostatic precipitator; 1A CA – PF ash from cyclone; $8A_{mix}$ – circulating fluidized bed (CFB) ash mixture; 8A EF1 – CFB ash from the 1st field of the electrostatic precipitator.

In general, the EC of PF OSA (excluding the 1A CA sample) leachates was 1.2-fold higher than that of CFB OSA leachates (Table 2). It was found that the mean EC was within the range of the published data for active landfill waste leachates [39] and higher in comparison with that of the leachates of alkaline pulverized coal combustion fly ashes [12, 14, 40, 41].

The main leaching characteristics of OSA samples established in this work were in good agreement with earlier published data on the leaching properties of different OSA (Table 2). The results of the present study demonstrated that the major ions in OSA leachates were represented by Ca^{2+}, K^{+}, Na^{+} and SO_4^{2-}. The leachable content of ions in PF ashes was more than 1.6-fold higher than in CFB ashes.

Recent studies showed that, in contact with water, alkaline combustion ash may be a source of potentially hazardous elements, including Zn [34, 40–43]. In this context, the concentration of Cd^{2+} and Zn^{2+} in the leachates was also measured and found to be below the detection limit, i.e. 0.02 mg/l and 0.01 mg/l, respectively.

Ca^{2+} and SO_4^{2-} ions were dominant in all leachates. The total leachable content of Ca^{2+} (the sum of the leachable content of the ion from the first and second extraction cycles) in OSA samples decreased as follows: 1A EF1 >

1A EF1-3 > 8A EF1 > 1A CA > $8A_{mix}$. In the case of PF OSA, the leachable content of major ions remained high through both extraction cycles (Table 2).

In the case of CFB OSA most of the Ca leaching took place already in the first cycle. Among PF ash samples the highest total leachable Ca^{2+} content, 25320 ± 50 mg/kg, was attributable to the 1A EF1 sample, whereas the leachable content of Ca^{2+} in the two CFB ash samples was close and did not exceed 16242 ± 33 mg/kg.

As presented in Table 2, the highest leachable content of SO_4^{2-} was found in 1A EF1-3 and 1A EF1 samples and the lowest, in the 8A EF1 sample: 1A EF1-3 > 1A EF1 > $8A_{mix}$ > 1A CA > 8A EF1.

In general, the leaching results obtained correspond to the content of free lime (leachable Ca^{2+}) and sulphates in OSA samples (Table 1). At the same time, the process is also affected by the porosity (expressed here by the parameter SSA) and size of ash particles. The low leachable Ca^{2+} content of 1A CA could be attributed to its low SSA and coarse particle size.

The phase composition, occurrence and quantity of Ca-containing components in ash play a significant role in the leaching behaviour of OSA samples. Our findings are in good agreement with published data on the leaching behaviour of alkaline combustion ashes [12, 40]. Izguierdo and Querol [12] demonstrated that leaching properties of ashes depend significantly on their content of Ca compounds. Due to their predominant surface association in fly ash and the marked solubility of most sulphate-bearing compounds, sulphur is the major soluble element in ash, along with Ca [12]. Ca is present in OSA in multiple forms, primarily as lime, anhydrite, calcite and within the glassy matrix [18, 19]. Thus, the leaching of Ca appears to be related to the phase composition of ash [3, 4].

Thorough studies [6, 7, 18, 19] have confirmed that under wet conditions hydration, carbonization, and subsequent transformation of OSA occur. The hydrous transformation of free lime (CaO), anhydrite ($CaSO_4$), secondary Ca(Mg)-silicate minerals and, especially in PF ashes, amorphous Al–Si glass phases control the solidification/cementation of ash, mainly by the formation of secondary Ca-rich hydrate phases and subsequently by the carbonation of portlandite [6].

The first stage of the hydration process is governed by fast and direct conversion of lime into portlandite (Eq. 1), followed by carbonation reactions to form calcite (Eqs. 2, 3) [3, 18, 19]:

$$CaO + H_2O = Ca(OH)_2 \tag{1}$$

$$CaO + CO_2 = CaCO_3 \tag{2}$$

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \tag{3}$$

However, the hydration and carbonation of CFB ash solids may be slower due to formation of Ca-sulfate shell [19]. In this case hydration of lime involves slow water diffusion through the sulphate layer and fast reaction with unreacted lime. It has been suggested that in case of PF ash carbonation of portlandite should be faster [18, 19].

During hydration, secondary calcium silicates react with water (Eq. 4) and silica or silicates can in turn react with $Ca(OH)_2$ (Eq. 6):

$$2Ca_2SiO_4 + 4H_2O = 3CaO\cdot2SiO_2\cdot3H2O + Ca(OH)_2 \tag{4}$$

$$CaSO_4 + 2H_2O = CaSO_4\cdot2H_2O \tag{5}$$

$$SiO_2 + Ca(OH)_2 + H_2O = CaO\cdot SiO_2\cdot2H_2O \tag{6}$$

Other important reactions in OSA hydration include anhydrite conversion to gypsum (Eq. 5) and the formation of ettringite (Eq. 7) and ferrites [15, 18, 19, 41]:

$$3Ca(OH)_2 + 2Al(OH)_3 + 3CaSO_4 + 26H_2O = Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O \tag{7}$$

Ettringite is a Ca,Al-sulphate hydrate, which is formed by the chemical interaction of the anhydrite/gypsum and residual dehydroxylated aluminosilicate clays and/or Al-Si glasses [19, 41, 44–47]. Ettringite is a primary phase always reported to be formed during the reaction of alkaline ash with water and may also capture a number of trace elements [12, 45, 46]. According to [19] ettringite does not form before all CaO has been converted to portlandite, and starts to transform into calcite.

Ettringite is stable in the presence of excess $CaSO_4$ and solid $Ca(OH)_2$ at pH = 10.7–12.2. At lower pH values ettringite is decomposed into sulfates and calcite (Eq. 8) [19]:

$$\begin{aligned}&Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O + 3CO_2 = \\ &\qquad 3CaCO_3 + 2Al(OH)_3 + 3CaSO4\cdot0.5H_2O + 27.5H_2O\end{aligned} \tag{8}$$

Hence, the obtained leaching characteristics of OSA samples may be determined by the different rate of transformation and formation of secondary components.

The leachates from BD were characterized by higher pH values and EC (Table 2) compared to OSA leachates. This could be attributed to the high content of readily soluble potassium salts. As expected, the content of leachable ions K^+, Na^+ and SO_4^{2-} of BD leachates was higher than that of OSA samples (Table 2). Nevertheless, the concentrations of Cd^{2+} and Zn^{2+} in the leachates were lower than the limit of detection (0.02 mg/l for Cd^{2+} and 0.01 mg/l for Zn^{2+}).

3.3. Leaching of OSA-based mortars

The leaching characteristics of PF and CFB OSA-based mortars with curing periods of 7, 28 and 91 days are presented in Figures 1–3. As expected,

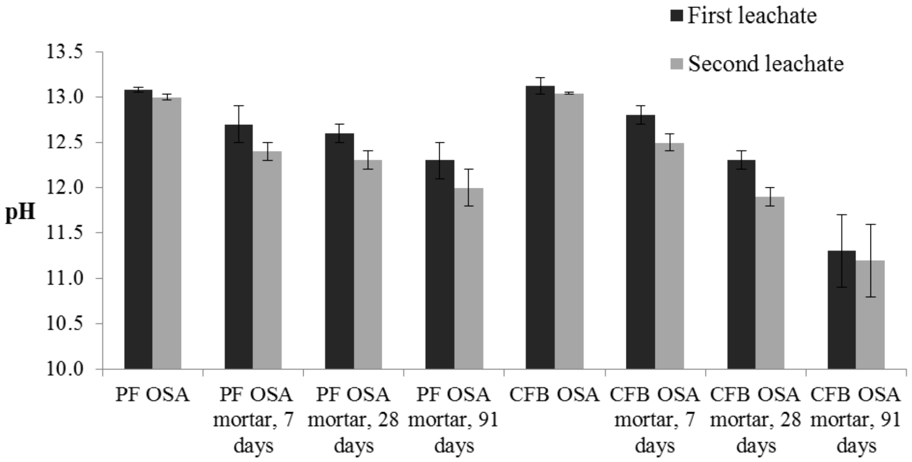

Fig. 1. Average pH values of the first and second leachates from initial pulverized-fired (PF) oil shale ash (OSA) (n = 3) and circulating fluidized bed (CFB) OSA samples (n = 2), and their respective OSA-based mortars after 7, 28 and 91 days of curing. Results represent the mean ± SD.

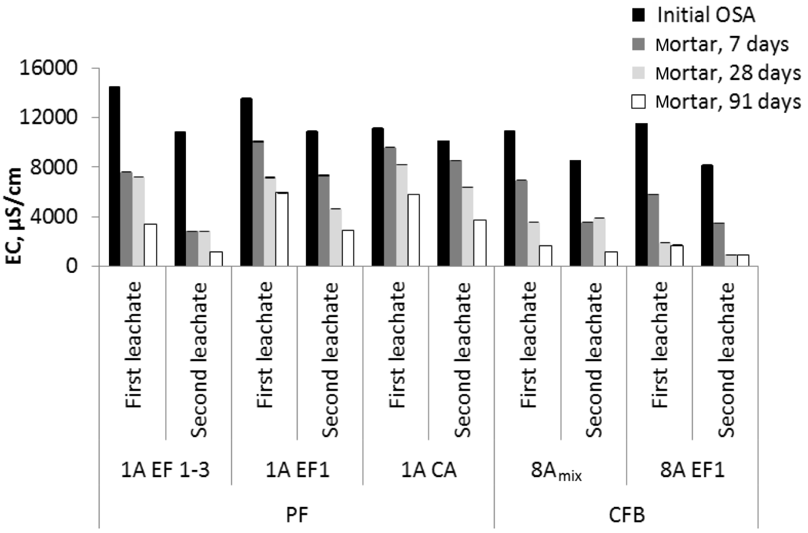

Fig. 2. Mean conductivity (EC) of the leachates from initial oil shale ash (OSA) samples and OSA-based mortars after 7, 28 and 91 days of curing. Results represent the mean ± SD of two parallel experiments.

1A EF1-3 – pulverized-fired (PF) ash from the 1st to 3rd fields of electrostatic precipitators; 1A EF1 – PF ash from the 1st field of the electrostatic precipitator; 1A CA – PF ash from cyclone; $8A_{mix}$ – circulating fluidized bed (CFB) ash mixture; 8A EF1 – CFB ash from the 1st field of the electrostatic precipitator.

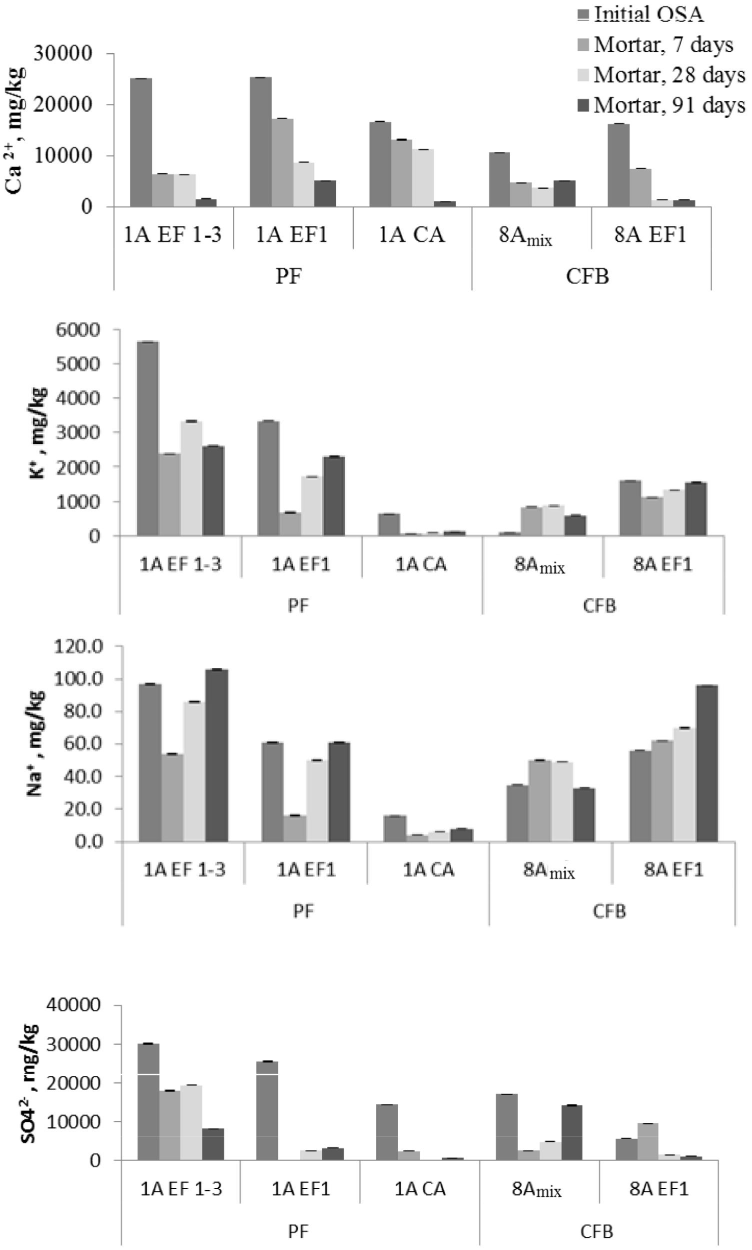

Fig. 3. Total leachable content of major ions from initial oil shale ash (OSA) samples and OSA-based mortars after 7, 28 and 91 days of curing. Results represent the mean ± SD of two parallel experiments.

the 1A EF1-3 – pulverized-fired (PF) ash from the 1st to 3rd fields of electrostatic precipitators; 1A EF1 – PF ash from the 1st field of the electrostatic precipitator; 1A CA – PF ash from cyclone; $8A_{mix}$ – circulating fluidized bed (CFB) ash mixture; 8A EF1 – CFB ash from the 1st field of the electrostatic precipitator.

the leachates were highly alkaline (Fig. 1) but their pH values as well as ECs decreased with increasing curing time and were lower than the corresponding data for the initial OSA (Figs. 1, 2). Based on EC values, the leachable fraction of inorganic compounds in PF OSA-based mortars was noticeably higher than that in CFB-based mortars (Fig. 2). At the same time, the leaching properties of each mortar depended on the specific characteristics of ash. Similarly to the results of OSA leaching tests, the leachates of mortars were also shown to contain mainly Ca^{2+}, K^+, Na^+ and SO_4^{2-}, which contributed to their highly alkaline pH values (Figs. 1, 3). The leachable content of major ions varied depending on the type of OSA and curing period (Fig. 3). For example, in the case of the 8A EF1-based mortar, a significant decrease in leachable Ca^{2+} and SO_4^{2-} was observed already after 28 days of hardening. The $8A_{mix}$-based mortar was characterized by a relatively low leachable content of Ca^{2+} while the leachable content of SO_4^{2-} increased in the course of hardening. In the case of the 1A EF1-3-based mortar, the leachable content of Ca^{2+} decreased 82 % during a curing period of 92 days. The 1A CA-based mortar was distinguished from other mortars by its higher content of leachable Ca^{2+} and lower content of leachable K^+ and SO_4^{2-} (Fig. 3). This observation may be explained by the high content of lime in 1A CA (Table 1) and, as a consequence, its quick lime-type hydration and low rate of hardening.

In general, the leachable content of ions in PF OSA-based mortars was more than twice that in CFB OSA-based mortars (Fig. 3). The concentration of Cd^{2+} and Zn^{2+} in all leachates was below the detection limit.

The experimental data gives clear evidence of the important role of specific OSA composition in the leaching behaviour of OSA-based mortars. Apparently, the leachable content of inorganic compounds is related to the quantity and form of CaO and secondary Ca minerals present in the mortars. Based on the obtained data the hydration processes and formation of secondary phases in PF OSA-based mortars may take longer than in CFB OSA-based mortars. Due to the incomplete calcination of carbonate phases and the effective sulphation of lime, CFB OSA contains less reactive CaO compared to PF OSA [4, 6]. Moreover, CFB OSA contains fewer Ca-silicate phases and is richer in quartz and anhydrite. Apparently in this case, the hydration type is mostly pozzolanic, but after 28 days of curing the process is hindered due to the lack of silicates and aluminates.

The chemical composition of elements, time, and pH all play an important role in controlling the mobility of elements in the solid material [12–14]. The results indicated that application of OSA in mortars leads to a decrease in readily soluble inorganic components and does not increase the leaching of hazardous Zn^{2+} and Cd^{2+}.

3.4. Leaching of OSA-based mortars: the effect of BD additive

The leaching test indicated that adding 1–10% BD to 1AEF1- and 8AEF1-based mortars did not have a significant effect on its leaching characteristics.

The results revealed that all the leachates were highly alkaline, but the mean pH and EC decreased during the 91-day curing period. The second leachates were characterized by slightly lower EC values (Fig. 4) compared to the first leachates. Adding BD to 1AEF1-based mortars resulted in a notable decrease in the EC values of the leachate, which were generally higher than those of 8AEF1-based mortars. Adding BD to OSA-based mortars also had some effect on the leachable content of Ca^{2+}, K^+, Na^+ and SO_4^{2-} ions (Fig. 5). In the case of 1A EF1-based mortars after 91 days of curing, the leachable content of Ca^{2+} decreased by about 30% and SO_4^{2-} increased by 24% with increasing BD content (Fig. 5). Adding BD to 8A EF1-based mortars increased the leachable content of Na^+, K^+ and SO_4^{2-} by 10%, 50% and 37%, respectively. The concentration of Cd^{2+} and Zn^{2+} in the leachates was below the limit of detection. However, a negligible concentration (0.112 mg/kg) of leachable Zn^{2+} was found in the 1A EF1-based mortar containing 1% BD after a curing time of 7 days. Apparently, adding up to 10% BD may affect the leaching properties of OSA-based mortars by adding more $CaCO_3$, Ca_2SiO_4, $KAlSiO_3$ and K_2SO_4 to the mix (Table 1).

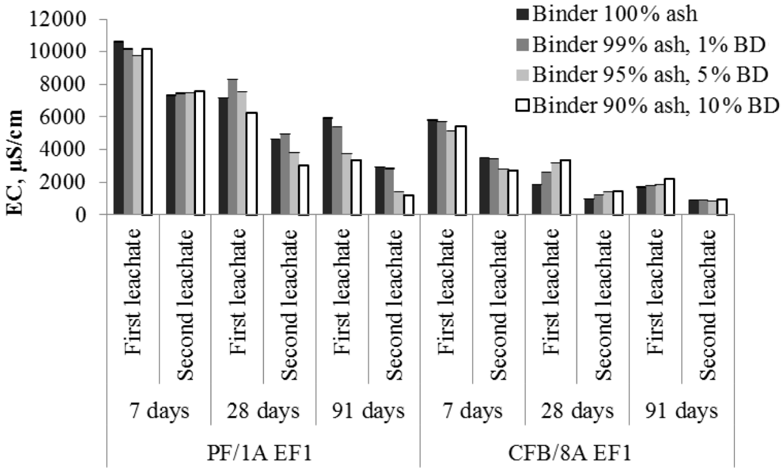

Fig. 4. Mean conductivity (EC) of the leachates from oil shale ash (OSA)-based mortars with 0–10% bypass dust (BD) added after 7, 28 and 91 days of curing. Results represent the mean ± SD of two parallel experiments.

PF/1A EF1 – pulverized-fired (PF) ash from the 1st field of the electrostatic precipitator; CFB/8A EF1 – circulating fluidized bed (CFB) ash from the 1st field of the electrostatic precipitator.

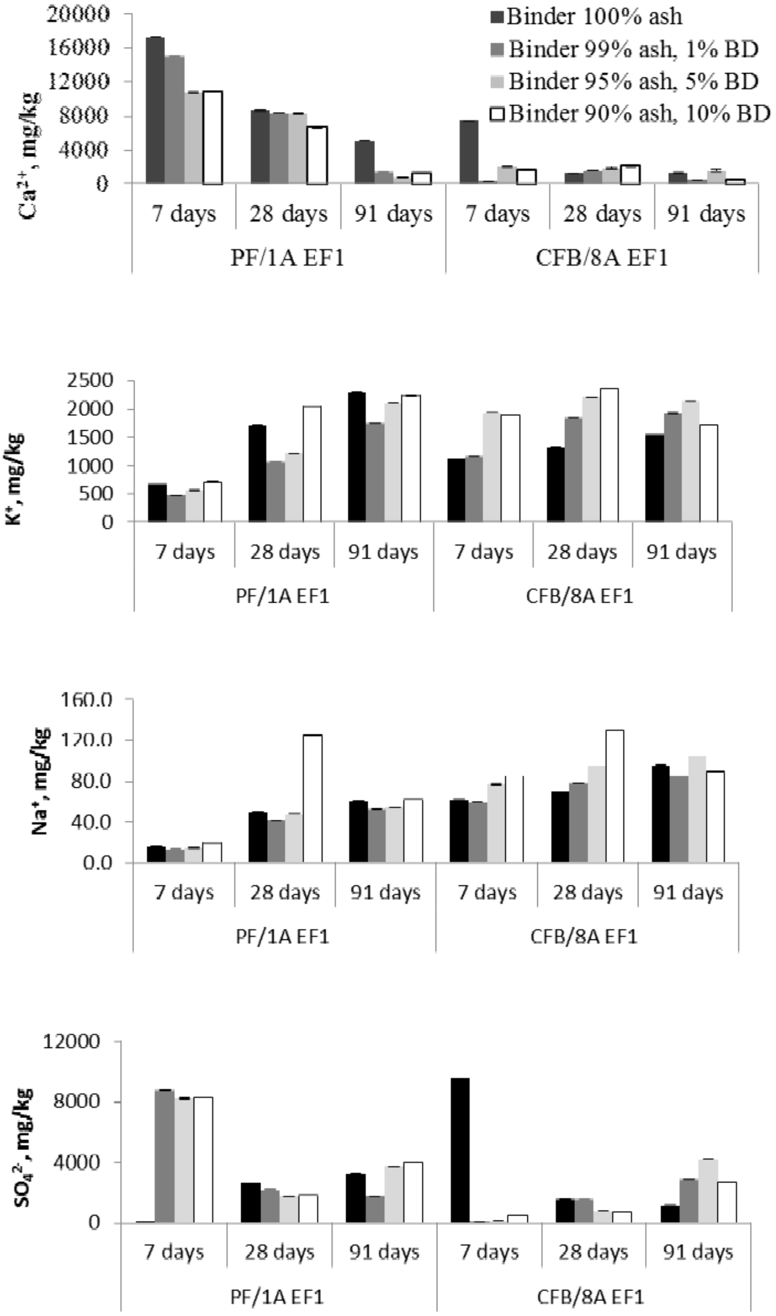

Fig. 5. Total leachable content of major ions from oil shale ash (OSA)-based mortars with 0–10% bypass dust (BD) added after 7, 28 and 91 days of curing. Results represent the mean ± SD of two parallel experiments.

PF/1A EF1 – pulverized-fired (PF) ash from the 1st field of the electrostatic precipitator; CFB/8A EF1 – circulating fluidized bed (CFB) ash from the 1st field of the electrostatic precipitator.

4. Conclusions

The leaching behaviour of different OSA samples and OSA-based mortars after curing periods of 7, 28 and 91 days was investigated. The diminishing effect of curing time as well as the increasing effect of 1–10% BD additive on the leachability of various soluble mineral components including harmful Cd^{2+} and Zn^{2+} was shown.

The leachable content of soluble inorganic components in the mortars decreased 2–4-fold on average during the experiment. The predominant ions in the leachates were represented by Ca^{2+}, K^{+}, Na^{+} and SO_4^{2-}. The PF OSA mortars were characterized by a noticeably higher (about 1.6-fold) content of leachable ions compared to CFB OSA mortars. The leachable content of major ions depended on the type of OSA and curing period. During the curing period the leachable content of Ca^{2+} and SO_4^{2-} decreased substantially, even as K^{+} and Na^{+}, in some cases, increased. During the experiments no leaching of Cd^{2+} and Zn^{2+} from OSA mortars was observed.

The mineral and phase composition of the respective OSA types from different fuel combustion technologies was the main factor affecting the leaching behaviour of their mortars, which is mainly connected to the content of CaO and formation of secondary Ca-compounds. Adding up to 10% BD to OSA-based mortars had a moderate effect on their leaching characteristics that depended on the type of OSA and curing time. The K_2SO_4 content in the BD sample caused some fluctuations in the leaching characteristics of K^{+} and SO_4^{2-}, while the mobility of potentially hazardous cadmium and zinc remained negligible.

So, in utilizing OSA in construction composites the rate and time course of processing as well as the formation and duration of secondary minerals that could change the composite leaching properties should be considered. The obtained results enlarge our knowledge about the environmental properties of OSA-based building materials, including backfilling composites for underground mining industry.

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