Electrochemical Investigation of Hazardous Metals Released from Fly Ash

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Abstract: The paper discusses the utilization of stripping voltammetric methods for the determination of Zn, Pb, Cr, Co and Ni in extracts from fly ashes. For this purpose, the most sensitive anodic stripping voltammetric (ASV) procedure for Zn and Pb quantification in acetic buffer has been selected. Traces of Ni, Co and Cr(VI) were determined by means of catalytic-adsorptive stripping voltammetry (CAdSV) with nioxime and nitrite (Ni and Co) or with DTPA and nitrate (Cr). It was observed that relatively high amounts of surface-active substances or other dissolved organic matter (DOM) present in the extracts severely interfered in the determination of the investigated metals ions by blocking the electrode surface and suppressing the stripping voltammetric response of metal ions, especially in ASV. Therefore, the methods of destroying DOM using ultraviolet irradiation or through their *in situ* removal via adsorption on the Amberlite XAD-7HP resin were examined and applied.

Keywords: Stripping voltammetry; Fly ash; Leaching.

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Introduction

Construction products may only be sold and used if they meet the standards comprised in Regulation (EU) no 305/2011 [1]. In the '*Basic Requirements for Construction Works*' section of Annex I, regulation lists not only the requirements traditionally embedded in

construction law, such as mechanical resistance and stability, safety in case of fire and safety and accessibility in use but also specifically refers to hygiene, health and environmental aspects. The possible emissions are classified into two categories:

1) Those released from construction products into the soil, ground water and surface water.

2) Emissions into indoor air.

The indicative list of regulated dangerous substances possibly associated with construction products is very long [2] and contains more than 70 regulated dangerous organic substances in the context of their release into soil, surface water and groundwater. Heavy metals such as Cr, Cu, Co, Mo, Se, V, Zn, Tl, Pb, Cd, Ni, Hg, Sn, Sb, As, Ba are included in the list. To predict interactions between the building material and the environment the following aspects should be considered:

a) Available content, total content analysis – information obtained after acid digestion of the samples.

b) Content of leachable species that could be released from construction products by leaching – information obtained based on the analysis of eluates.

The leaching of soluble constituents upon contact with water is regarded as the main mechanism of release of dangerous substances, and it is controlled by the kinetics of the penetration of water and aggressive agents into concrete. The movement of chemical species within the material and the leaching of certain chemicals are closely linked to concrete diffusivity and durability.

Fly ash is a product of burning finely ground coal in a boiler to produce electricity. In power plants, it is removed from the exhaust gases primarily by electrostatic precipitators, or baghouses and secondarily by scrubber systems. Currently, the term 'waste' is not used for recyclable materials such as fly ash, and instead more 'neutral' expressions such as 'secondary raw material' or 'by-product' are common [3]. Every year in Poland, 110 million tons of carbon are burned in power stations and at the same time 4 million tons of fly ash are produced, which constitutes about 25% of inflammable residue formed during combustion [4]. Coal fly ash is an artificial pozzolan and reacts with calcium hydroxide, the byproduct of cement hydration, to form products similar to cement hydration, Ca–Si gels, which determine the concrete strength. The reactions between fly ash and calcium hydroxide are called pozzolanic reactions. Due to pozzolanic activity, fly ash is used as an additive to Portland cement or as an admixture for concrete. The major components in fly ash are silica (SiO_2),

alumina (Al_2O_3), iron(III) oxide (Fe_2O_3) as well as carbon, calcium (in the form of CaO or gypsum), magnesium, and sulphur.

Although many metals are present in the form of oxides, there are also significant amounts of metal chlorides, metal sulphates, and metal carbonates. Aside from reducing the consumption of natural resources and eliminating the need to dispose of fly ash in a landfill, incorporation of fly ashes into concrete also imbues it with some positive properties. Fly ash limits alkali-silica reactions, which are damaging to concrete, and increases concrete's resistance to freezing. The addition of relatively high amounts of fly ash (ca. 60 %) to concrete does not damage the passive Fe_2O_3 layer that protects steel reinforcements in concrete. The microstructure of cement paste containing fine fly ash is more compact in comparison to conventional paste (lower capillary porosity, higher content of gel pores) and such pastes are characterized by higher compressive strength and higher resistance to chemical attack [5,6].

To assess the potential of ash constituents to leach into the environment, its water extracts should be analysed. Construction products may contain Cr, Cu, Co, Mo, Se, V, Zn, Tl, Pb, Cd, Ni, Hg, Sn, Sb, As, Ba, and their release should therefore be assessed [2]. The concentrations of listed elements in eluates are usually low, at ppb or sub-ppb levels, with the exception of Cr – reaching a level of several dozen ppb – and Mo, present in a concentration of ca. 200 ppb). Detection limits at sub-ppb levels are routinely achieved for most of these elements, both with spectrometric methods (*e.g.* ICP-MS) and stripping voltammetric procedures. Methods used for the analysis of substances in natural water (*e.g.* ICP techniques) may not be appropriate for construction product extracts containing high concentrations of salts due to their high ionic strength. The dissolved salts present in eluates can deposit on the tip of pneumatic nebulizers and on interface skimmers, reducing the orifice size and the instruments' performance. The content of salts in concrete extracts, estimated via conductivity measurements, exceeds 0.1 %, and it is close to the upper value of salt concentration, *i.e.* 0.2 %; above this level, precipitating solids clog the nebulizers.

Another potential interference is the presence of high concentrations of Ca, Mg and Fe. A high concentration of Ca disturbs plasma generation [7], and makes it impossible to obtain reliable concentration values without using the empirical coefficient. The total concentrations of Ca(II) and Mg(II) in concrete eluates reach 0.5 g/l and at such alevel may interfere with the determination of Zn, Cd, Co, Cr, and V. High ionic strength, on the other hand, does not disturb voltammetric determination, and it may even be increased deliberately to obtain high conductivity of the tested samples.

The methods applied for the quantification of metal traces are usually stripping techniques, such as stripping voltammetry (SV) and chronopotentiometry (CPS). Stripping voltammetry is a two-step technique.

The additional, preliminary step is the *in-situ* deposition of a chemical species onto the electrode surface at a constant potential. This preconcentration step can involve adsorption, amalgamation (Hg electrodes), or the formation of compounds between the electrode material and the targeted substances.

The aim of this project is the application of voltammetric techniques for the assessment of the release of the selected toxic metals from fly ash used as a component of building materials into environment.

Experimental

Chemicals

The following reagents (analytical grade, POCH, Poland) were used without further purification: 30% H_2O_2, CH_3COOH, $CH_3COONa \cdot 3H_2O$. Nioxime and $NaNO_2$ (analytical grade, POCH, Poland) were crystallized from ethanol and water, respectively. Suprapur HCl, NH_3 and NH_4Cl (Merck, Germany) were used for samples acidification and preparation of ammonia buffer. Amberlite XAD-7HP resin (Sigma, USA) was washed four times with water deionized water and dried up at a temperature of 50 °C. All solutions were prepared using deionized water (Millipore Simplicity UV, Millipore Corporation, USA).

Equipment

Electrochemical measurements were performed using a μAutolab (GPES 4.9 software) potentiostat (Ecochemie, Netherlands) with a standard three-electrode configuration. A coil of platinum wire served as the counter electrode, and an Ag/AgCl electrode (3 M KCl) (Metrohm, Switzerland) was used as the reference one.

The working electrode of 1.9 mm^2 area was control growth mercury drop electrode (CGMDE), (MTM, Poland). Before recording voltammograms oxygen was removed from examined solution by argon flow (7 minutes). Photolysis was performed using UV digestion system with 150 W lamp (Mineral, Poland).

The morphology of the deposits was evaluated using a Nova NanoSEM 200 (FEI company, USA) scanning electron microscope (SEM) with elemental energy dispersive X-ray microanalyser. Each fly ash sample was characterized by randomly selecting 3–4 fields of view and examining all the fly ash particles observed within the selected fields.

Extraction Procedure

The extraction procedure was performed according to EN 12457-2:2002 *One stage batch test at a liquid to solid ratio of 10l/kg for materials with particle size below 4 mm.* Briefly, 90 g of ash was placed in dry polypropylene bottle and mixed with 900 ml of distillated water (room temperature). Next, the bottle was screwed on and placed in rotary agitator (extractor) (36 rpm, bottles placed at an angle of 45 degrees to the axis of rotation) for 24 h. After mixing, the samples were filtrated, the pH and conductivity was measured. The fraction of extract for voltammetric determination was acidified to pH 2 using concentrated HCl Suprapur (Merck).

Elimination of Organic Matter and Voltammetric Procedure

The voltammetric determination of Cr(VI) in fly ash extracts was possible without any additional pretreatment. Only the dilution of the analyzed sample was required. However, the voltammetric quantification of the Zn, Pb, Cd, Ni and Co had to be preceded by photolytic decomposition of dissolved organic matter (DOM) or its adsorption on Amberlite XAD-7HP resin to eliminate the negative influence of the DOM on the results of the voltammetric experiments. The acidified extract samples were spiked with 30% H_2O_2 (1 µl perhydrol per 1 ml of sample) and exposed to UV in digesting system for 2 h or more when required. After digestion the cooled down samples were diluted with supporting electrolyte and examined voltammetricaly.

The Amberlite XAD-7HP was washed four times in bi-distilled water and dried up at 50 °C prior to analysis. When Amberlite XAD-7HP was used the 0.5 g of resign was added to voltammetric vessel containing 10 ml of examined solution. After that the stirring was performed for 5 minutes. The mixture was not filtrated; the voltammograms of sample and sample after addition of standards were recorded with resin in the vessel.

Sample Characteristics

The fly ash samples originated from thermal power stations in Poland. The first batch of fly ashes were sampled from the electrostatic precipitator of a bituminous coal-fired boiler operating at a temperature of 1350 °C, this batch is referred to in this study as sample A. The second sample, labeled B, came from an electrostatic precipitator attached to a fluidized bed lignite-fired boiler operating at a temperature close to 850 °C. The main oxide components of the investigated fly ashes were (in an order corresponding to amount): SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, MgO, TiO_2 and Na_2O – in the case of sample A – and SiO_2, CaO, Al_2O_3, SO_3, Fe_2O_3, MgO, Na_2O, K_2O and TiO_2 – for sample B. The loss on ignition (LOI) at 1000 °C of the samples was 5.2 % and 2.6 % for sample A and B, respectively (Table I).

Table I: *The characterization of ash samples.*

	Solid sample			Eluate		
	Total carbon (TC) (%)	Total organic carbon (TOC) (%)	The loss on ignition (LOI) at 1000 °C (%)	Density at 22 °C (g/ml)	pH	Conductivity (mS cm^{-1})
A	4.2	0.4	5.2	1.011	11.36	1.608
B	4.2	0.1	2.6	1.003	12.62	8.279

Results and Discussion

Microscopic Analysis of Fly Ash

The morphology of fly ash particles depends on boiler type, combustion temperature and cooling rate. Striking differences are visible when comparing images A and B shown in Figure 1. The fly ash A originating from conventional burning consisted of isolated spherical grains of different diameters and few agglomerates. The spherical grains did not occur when fly ash from fluidized bed (B) was examined. The microscopic images also reveal that fly ash A contains a substantial amount of irregularly shaped spongy particles of unburned carbon (Figure 1 B). In the case of sample B the carbon particles were sparse. The abundance of unburned carbon revealed in sample A through microscopic examination was confirmed by means of total organic carbon determination. In the case of sample B the TOC was 30 times smaller than that obtained for ash A.

Organic matter may interfere during voltammetric studies, because some fraction of the organic compounds present in fly ash can be extracted to a water phase during leaching. The presence of organic compounds in samples undergoing voltammetric analysis to determine their metal content could cause serious problems, such as: a) blockage of the surface of the electrode as a result of their adsorption on the electrode surface, b) adsorption – desorption processes contributing to measured current, resulting in distorted voltammograms, c) undesirable complexation that could mask the voltammetric signals of the targeted ions, and d) reduction – oxidation processes observed at potentials similar to that of the analyte.

Elimination of Interferences from Organic Matter

The DP anodic stripping voltammetric curves recorded for the leaching solution of the bituminous coal-fired boiler fly ash sample A (Figure 2I) in the potential range from −1.2 V to −0.2 V show several signals, but none of them is clearly related to the oxidation of target metals. The signals observed in the vicinity of the Zn peak potential are distorted and non-reproducible. The other peaks are very wide and do not look like typical, narrow metal oxidation peaks. The inevitable presence of surface-active substances (SAS) or other constituents of natural organic matter interferes with the stripping voltammetric determination of target metals by partially or even entirely blocking the surface of the working electrode. This problem has been particularly relevant for conventional fly ashes, in which organic matter concentrations can reach several % in solid samples (extract A).

Thus, the main efforts were focused on the elimination of the influence of dissolved organic matter (DOM), including organic surface-active substances (SAS) that adsorb at the electrode surface, and disturb or even prevent the ASV determination of Zn, Cd and Pb or the CAdSV determination of Ni and Co. Consequently, two different approaches to eliminating interferences from DOM were tested: 1) decomposition of DOM by means of UV-irradiation and 2) adsorptive removal on the Amberlite XAD-7HP resin added directly to the voltammetric vessel [8-11]. Unfortunately, after UV photolysis the interfering signals were still present, even though when exposition to UV was prolonged to 6 hours and hydrogen peroxide was added. The elimination of organic matter by adsorbing it on the Amberlite XAD-7HP resin was therefore tested [8-11].

A 0.6 g batch of the resin was added directly to the voltammetric vessel (10 ml of solution) containing the sample diluted (1:1) with acetic buffer. The mixture was stirred for 5 minutes and then underwent voltammetric measurements. The DPASV voltammograms

recorded in the presence of the added resin are shown in Figure 2II; see overleaef. The voltammograms are free from interfering signals and thanks to this, two peaks can be observed: a sensitive, narrow peak of Zn oxidation (E_p = −1.05 V vs. ref.), and much smaller peak of Pb (E_p = −0.51 V).

After the addition of Amberlite XAD-7HP, the determination of Zn, Pb and Cd was possible, but the presence of the relatively large volume of resin in the voltammetric vessel slowed down the stirring and impaired the efficiency of analyte accumulation; consequently, a very long accumulation time had to be applied (> 500 s for Pb). This observation forced us to resume UV mineralization.

A
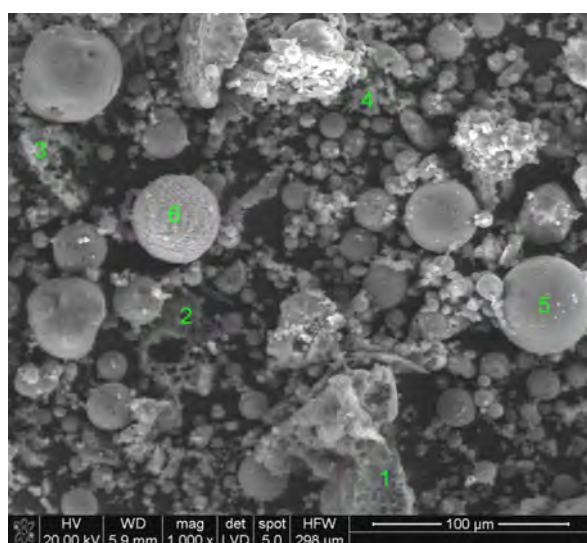
The distribution of elements (EDS analysis)

(1) Carbon (100%);

(2) Carbon (100%);

(3) Carbon with small amount of silicone, aluminium and oxygen containing compounds;

(4) Carbon with higher than in case of point 3 amount of silicone, aluminium and oxygen containing compounds;

(5) Silicone, aluminium, oxygen and potassium containing compounds with small amount of carbon;

(6) Iron oxide.

B
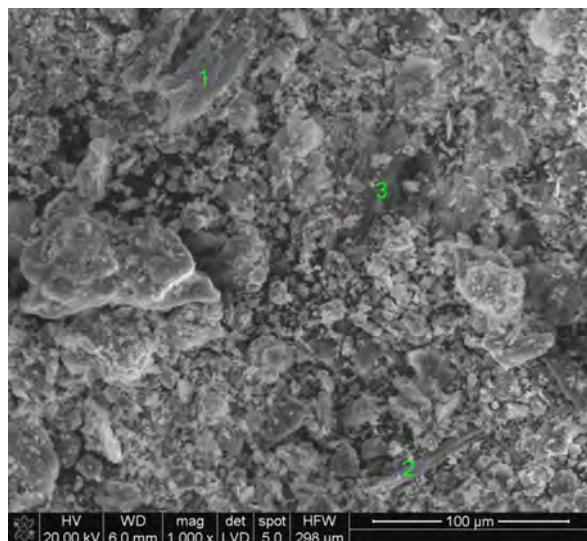
(1) Aluminium, silicone, oxygen, sodium, calcium compounds containing small amount of carbon;

(2) Aluminium, oxygen, silicone, calcium, sodium containing compounds containing small amount of carbon

(3) Carbon and oxygen, aluminium, silicon, calcium and sodium containing compounds

Fig. 1: *SEM images of fly ash samples A and B.* Right column: the distribution of components in fly ash grains assessed on the basis of SEM/EDS spectra; the elements are listed in order of decreasing abundance.
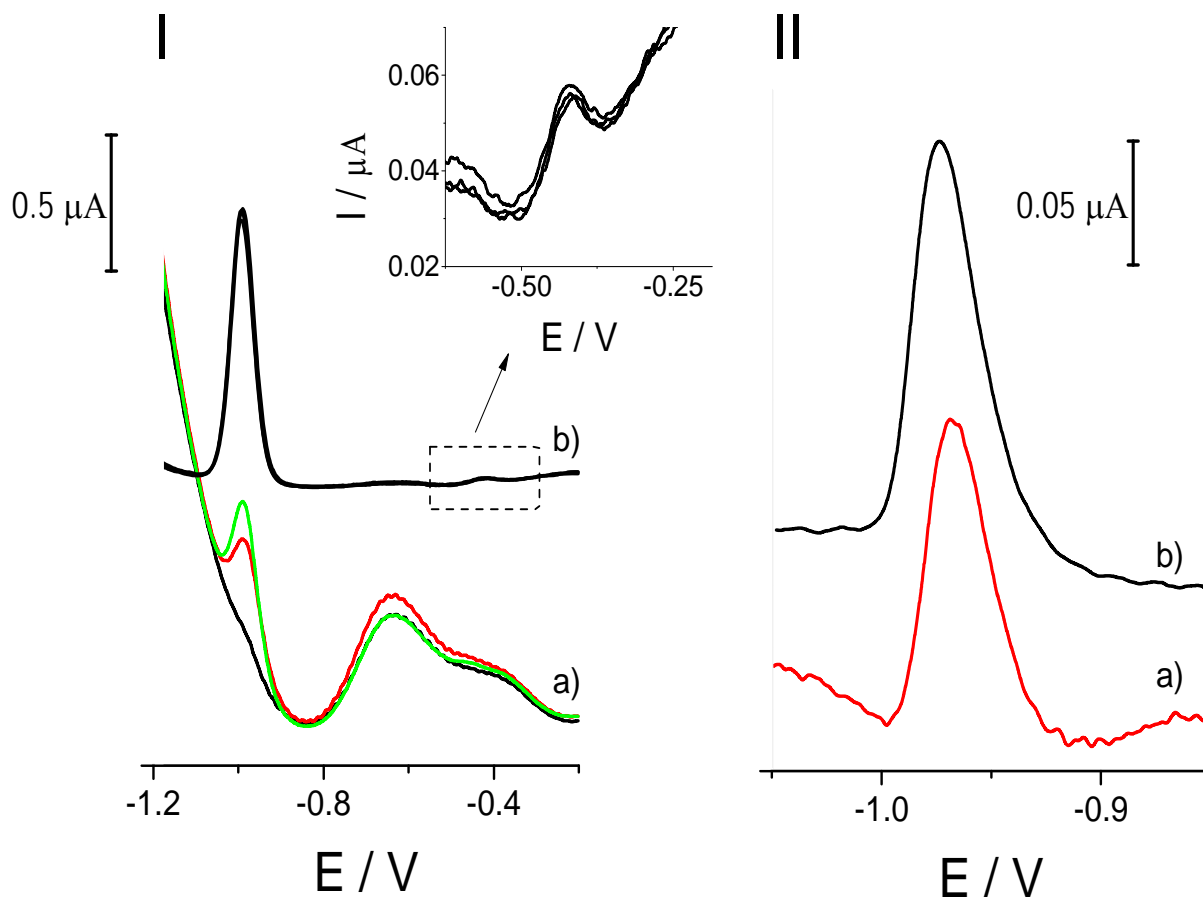
Fig. 2: (I): *DPV voltammograms recorded in fly ash extract diluted (2 times) with acetic buffer in the absence* (a) *and in the presence* (b) *of Amberlite XAD-7HP (0.5 g of resin added to 10 ml of solution)*. Electrolyte: 0.1 M acetic buffer, pH 4.5. Instrumental parameters: $E_{acc} = -1.2$ V, $t_{acc} = 30$ s, $t_{eq} = 10$ s, $\Delta E = 50$ mV; (II): *DPV voltammograms recorded in fly ash extract diluted (20 times) with ammonia buffer before (a) and after 2 hours of UV photolysis (b)*. Electrolyte: 0.1 M ammonia buffer, pH 9.2; $5 \cdot 10^{-5}$ M nioxime. Instrumental parameters: $E_{acc} = -0.85$ V, $t_{acc} = 30$ s, $t_{eq} = 10$ s, $\Delta E = 50$ mV

Finally, it was established that 24 hours of UV photolysis in the presence of hydrogen peroxide (1 µl of H_2O_2 per 1 ml of sample) allowed the determination of Pb and Cd.

The interferences were also observed when adsorptive stripping voltammograms (AdSV) were recorded (Fig. 2II), but they were less severe than those observed in ASV experiments. The background line was undulated, but the peak of Ni was distinct. After 2 hours of UV-irradiation the measured peak of Ni was 1.4 times higher and the background line was free from oscillation.

Determination of Metals in Fly Ash Extracts

Zn(II) and Pb(II) Determination. In the course of the anodic stripping voltammetric determination of Zn and Pb, the formation of amalgams is exploited to accumulate the analyte into the mercury electrode. The voltammetric determination involves two steps: the preconcentration of a metal phase into liquid mercury at negative potentials and the subsequent oxidation of metal phase species during an anodic potential sweep.

Voltammetric Procedure. The voltammetric determination of Zn and Pb in sample A (bituminous coal-fired boiler) was preceded by 24 hours of irradiation in the presence of hydrogen peroxide. In the case of sample B (a fluidized bed lignite-fired boiler) the less aggressive mineralization was sufficient, 2 hours of UV exposition (Pb) or adsorption on Amberlite XAD-7HP resin (Zn). The 5 ml of sample were mixed with 1 ml 1 M acetic buffer (pH = 4.5) and 4 ml distilled water. The ASV curves of Zn were recorded in differential pulse (DP) mode and following instrumental parameters were involved: preconcentration with stirring at E = −1.2 V for 30 s, 5 s rest time (without stirring), differential pulse scan from −1.2 V up to −0.7 V; potential step high = 2 mV, potential pulse 50 mV. During the Pb determination the accumulation potential was switch to −0.7 V to minimize the adsorption of traces of organic substances present in the sample despite the UV-irradiation of sample.

The resulting voltammograms are shown in Figure 3. The signals of Zn (E_p = −0.99 V) and Pb (E_p = −0.386V) are distinct, symmetric and reproducible (RSD for 10 voltammograms 6.4 % and 1.4 % for Zn and Pb, respectively). The addition of Zn(II) and Pb(II) standard caused the linear increase of the peaks height. The results of Zn and Pb determination obtained by standard addition method are collected in Table II.

Ni(II) and Co(II) Determination. For the simultaneous determination of Co and Ni traces in the leaching solutions of the investigated fly ashes, the most sensitive and selective catalytic-adsorptive stripping voltammetric procedure with nioxime and nitrite was selected [12-15].

The significant sensitization of the Ni- and Co voltammetric signals in the above procedure is a result of two (in the case of Ni) or even three (in the case of Co) effects the reduction of Ni and Co nioximate complexes with the participation of dioxime ligands [12,16], the adsorptive preconcentration of Ni-nioxime and Co-dioxime complexes onto the surface of the working electrode (HMDE or various solid electrodes) [12,17], and the catalytic reduction of nitrite anions induced by the reduction of Co-dioxime complexes [12,13,15].
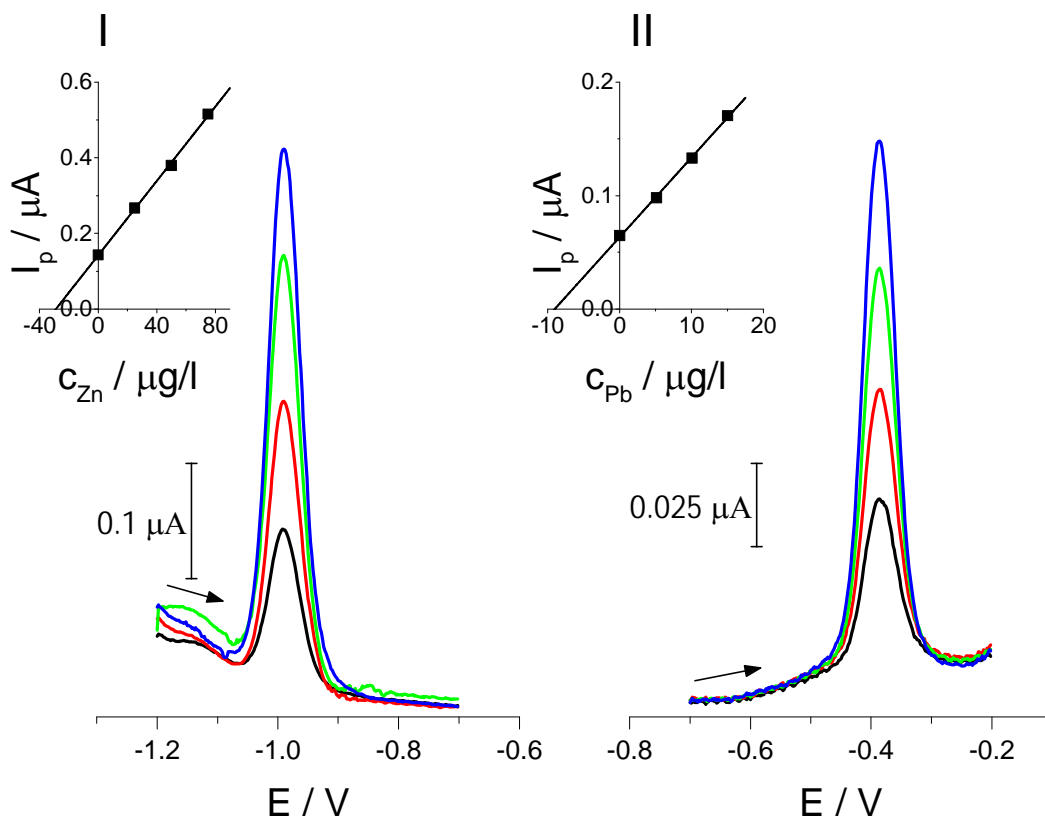
Figure 3. *The determination of zinc(II) and lead(II) in diluted (2 times) fly ash extract B.* Electrolyte: 0.1 M acetic buffer, pH 4.5. Electrolyte: 0.1 M acetic buffer, pH 4.5. Instrumental parameters: Zn: $E_{acc} = -1.2$ V, $t_{acc} = 30$ s, $t_{eq} = 5$ s, $\Delta E = 50$ mV; Pb: $E_{acc} = -0.7$ V, $t_{acc} = 90$ s, $t_{eq} = 5$ s, $\Delta E = 50$ mV. Sample after 2 hours of UV photolysis. Insets: standard additions plots.

Voltammetric Procedure. The voltammetric determination of Ni and Co in sample B was preceded by 24 hours of UV-irradiation in the presence of hydrogen peroxide and 2 hours of UV exposition without hydrogen peroxide). A 0.5 ml batch of the sample was mixed with 2 ml of 0.5 M ammonia buffer (pH = 9.2), 7.5 ml of distilled water, and 0.05 ml of 0.01 M nioxime. The voltammograms of Ni were recorded in DP mode and the following instrumental parameters were applied: preconcentration with stirring at E = -0.85 V for 30 s, 5 s of rest time (without stirring), differential pulse scan from −0.85 V up to −1.05 V, potential step high = 2 mV, potential pulse = 50 mV.

The Ni peaks ($E_p = -0.966$ V) shown in Figure 4I are well-separated from the background and reproducible (RSD 2.4 % for 10 voltammograms). The results of Ni determination obtained by means of the standard addition method are collected in Table II.

Table II: *Leachate characterization for the ash sample A and B* (the recovery of metals ions spiked to the leached solution ranged from 90 % to 107 %).

Component	Concentration in eluate A (µg/l)	Contents (mg/kg dry substance)	Concentration in eluate B (µg/l)	Contents (mg/kg dry substance)	Limit value	Classification
Pb(II)	$15 \pm 2^{**}$	0.15	$17 \pm 1^{*}$	0.17	$0.5^{(a)}$	Inert
Zn(II)	$41 \pm 5^{**}$	0.41	$50 \pm 6^{***}$	0.5	$4^{(a)}$	Inert
Ni(II)	$6 \pm 2^{**}$	0.06	$19 \pm 2^{*}$	0.19	$0.4^{(a)}$	Inert
Co(II)	$0.3 \pm 0.01^{**}$	0.003	$0.20 \pm 0.01^{*}$	0.002	-	-
Cd(II)	Below LOD	-	Below LOD	Below LOD	$0.04^{(a)}$	Inert
Cr(VI)	113 ± 3	0.11	155 ± 3	0.16	$0.1^{(b)}$	Higher than maximum allowable concentration

Legend:

* - After 2 h of UV exposition.

** - After 24 h of UV exposition of sample spiked with H_2O_2.

*** - After adsorption on Amberlite XAD 7HP.

$^{(a)}$ mg/kg dry substance - Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of Annex II to Directive 999/31/EC (2003/33/EC).

$^{(b)}$ mg/l - Regulation of the Minister of the Environment on the conditions that must be met to discharge wastewater to water or land, and on the substances that are particularly hazardous for aquatic environments of July 24th 2006.

In the case of Co determination, the supporting electrolyte used for Ni determination was enriched with $NaNO_2$. 2 ml of sample were mixed with 2 ml of 0.5 M ammonia buffer (pH = 9.2), 6 ml of distilled water, 0.05 ml of 0.01 M nioxime and 0.25 g of $NaNO_2$. The DP voltammograms of Co were recorded using the following instrumental parameters: preconcentration with stirring at E = −1.0 V for 30 s, 5 s of rest time (without stirring), differential pulse scan from −1.0 V up to -1.2 V, potential step high = 2 mV, potential pulse = 50 mV. The addition of $NaNO_2$ to ammonia buffer containing nioxime caused the appearance of clearly-defined, reproducible (RSD 3.3 % for 10 voltammograms) peak of Co (E_p = −1.132 V), enabling the determination of Co at sub-ppb level (Figure 4II). The results of Co determination obtained by the standard addition method are also collected in Table II.
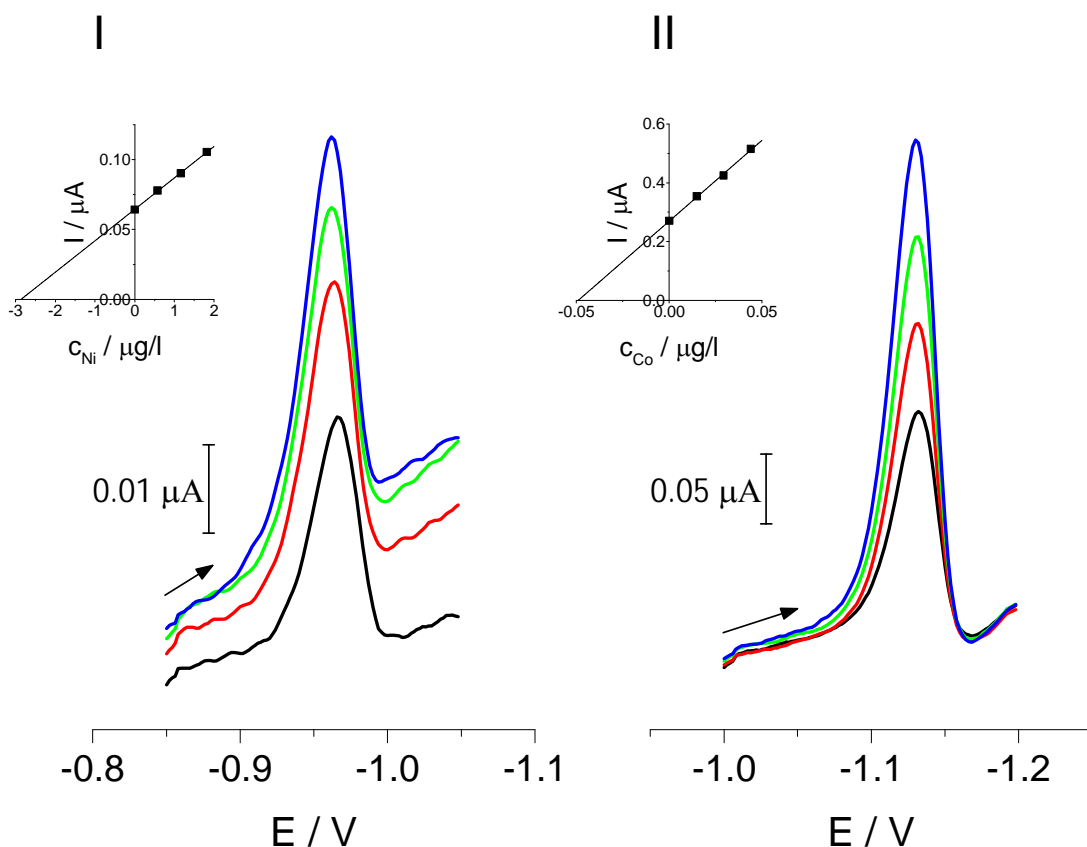
Fig. 4: *The determination of Ni (I) and Co (II) in fly ash extract B*. Ni: sample diluted 20 times, electrolyte: 0.1 M ammonia buffer, pH 9.2, 0.05 mM nioxime, instrumental parameters: E_{acc} = −0.85 V, E_{acc} = 30 s, t_{eq} = 5 s, E_s = 2 mV, ΔE = 50 mV. Co: sample diluted 5 times, electrolyte: 0.1 M ammonia buffer, pH 9.2, 0.05 mM nioxime, 0.36 M NaNO$_2$; instrumental parameters: E_{acc} = −1.0 V, E_{acc} = 30 s, t_{eq} = 5 s, E_s = 2 mV, ΔE = 50 mV. Insets: standard additions plots.

Cr(VI) Determination. The procedure for Cr utilizes diethylenetriaminepentaacetic acid (DTPA), which forms a species with the Cr(III) that adsorbs on a hanging mercury drop electrode (HMDE). At about -0.050 V, the Cr(VI) present in the examined solution is reduced irreversibly to Cr(III), which immediately forms a complex with DTPA present in excess on the electrode surface due to its adsorption. The Cr(III)-DTPA complex is subsequently reduced to Cr(II) at about -1.2 V in a quasireversible reaction. Reoxidation to Cr(III) is initiated by nitrate, reduced itself to nitrite. This catalytic redox cycle considerably increased the analytical signal of Cr(VI) [18-21].

Voltammetric Procedure. 2.5 ml of 1 M KNO_3 were mixed with 1 ml of 1 M $CH_3COOH-NH_3$ (pH = 6.2), 1 ml of 0.1 M DTPA, 5 ml of distilled water, and 0.5 ml of analyzed sample. The voltammetric measurements were performed after 40 min of contact between the sample and the components of supporting electrolyte.
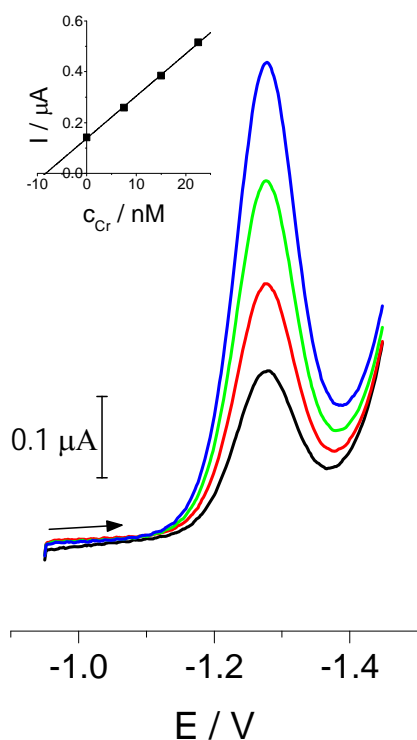

Figure 5. *DPV voltammograms recorded in fly ash extract B without and after Cr(VI) standard additions.* Examined solution: sample diluted 400 times, 0.1 M acetic buffer, 0.025 M DTPA and 0.25 M KNO_3. Instrumental parameters: E_{acc} = −1.2 V for 30 s, t_{eq}= 5 s, E_s = 2 mV, ΔE = 50 mV. Inset: standard additions plot.

The voltammograms were recorded in differential pulse mode and the following instrumental parameters were applied: preconcentration with stirring at E = −0.95 V for 15 s, 5 s of rest time (without stirring), differential pulse scan from −0.95 V up to −1.45 V, potential step high = 2 mV, potential pulse = 50 mV. The determinations of Cr(VI) were performed in samples that had not been exposed to UV light.

The Results. Figure 5 shows the voltammograms obtained in the diluted extract obtained from sample B. The well-shaped, distinct peak of Cr(VI) was observed at a potential of -1.28 V. The addition of the Cr(VI) standard caused a linear increase in the peak's height. The results of Cr(VI) determination obtained by means of the standard addition method are collected in Table II.

Conclusions

The present work demonstrated that stripping voltammetry exploiting the hanging mercury electrode is suitable technique for evaluating the release of dangerous metals such as Zn, Pb, Cd, Ni, Co and Cr(VI) from fly ash and into ground water, marine waters, surface waters, or soil. The performed experiments proved that UV pretreatment or the use of the Amberlite XAD-7HP resin were sufficiently effective at eliminating the interfering dissolved organic matter. It is expected that the level of organic matter present in the fly ash water extracts will increase in the near future because of co-combustion of alternative fuels in boilers designed for coal burning. The introduction of alternative fuels may, however, impair boiler performance and the amount of unburned matter in fly ash (and thereby in its water extracts) may be elevated.

The presented results show that voltammetry preceded by UV photolysis or adsorption of organic matter could be successful in the assessment of the release of dangerous substances from fly ash. The release of dangerous substances is a problem of great economic significance, as under Regulation (EU) no 305/2011 the leaching assay belongs among the basic requirements that construction works must satisfy. The described voltammetric procedure coupled with the elimination of organic matter from extracts could be implemented in the future to achieve more environmentally friendly voltammetric protocols exploiting amalgams, mercury-free metallic films, and screen-printed electrodes. Their application will further shorten and simplify the course of voltammetric determination of targeted metals.

Acknowledgements

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