



Heavy metal migration during electroremediation of fly ash from different wastes—Modelling

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ARTICLE INFO

Article history:

Received 26 May 2009

Received in revised form

13 September 2009

Accepted 5 October 2009

Available online 12 October 2009

Keywords:

Electrodialytic process

Fly ash

Nonlinear biregressional design

Kinetic parameters

ABSTRACT

Fly ash is an airborne material which is considered hazardous waste due to its enrichment on heavy metals. Depending on the waste from which they are originated, fly ash may be further valorised, e.g. as soil amendment or concrete and ceramics adjuvant, or landfilled, when defined as hazardous material. In any case, heavy metal content has to be decreased either for fly ash valorisation or for complying with landfill criteria. The electro-dialytic (EDR) process is a remediation technique based on the principle of electrokinetics and dialysis, having the aim to remove heavy metals from contaminated solid media. EDR was here applied to fly ashes from the combustion of straw (ST), from the incineration of municipal solid waste (DK and PT) and from the co-combustion of wood (CW). A statistical study, using *F* tests, Bonferroni multiple comparison method and a categorical regression, was carried out to determine which variables ("Ash type", "Duration", "Initial pH", "Final pH", "Acidification" and "Dissolution") were the most significant for EDR efficiency. After establishing these, the selected variables were then used to characterize some kinetic parameters, from metals migration during EDR, using a biregressional design. Cd, Cr, Cu, Ca and Zn migration velocity and acceleration to the electrodes (anode and cathode) were then considered. Cd and Cu migration to the cathode were found to be significantly influenced by "Ash type", "Duration", "Final pH" and "Dissolution".

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1. Introduction

Incineration is a high-technological and effective waste treatment technique, with a rising trend. With EU policies stimulating incineration as waste management solution [1–4] and having a target of 15% renewable energy out of the total energy production until 2010, biomass (wood, straw and certain crops) combustion is rising. This means increase of incineration residues such as fly ash.

Fly ash is considered to be a hazardous material due to its toxicity [3] and enrichment with volatile contaminants and heavy metals. As hazardous waste, it is current practice to stabilize fly ash with raw material for subsequent disposal in landfill. However, depending on fly ashes fuel origin, they may be reused for instances as soil amendment, in geotechnical, or concrete applications [5,6], particularly after reduction or total removal of contaminants. The electro-dialytic process (EDR) is a remediation technique first described for heavy metal contaminated soil [7–9]. The method combines an electric DC field as cleaning agent with ion-exchange

membranes, which allow the regulation of ion fluxes. The design, developed at the Technical University of Denmark, consists of a cell divided in three compartments, (I) anode compartment, (II) central compartments, where the contaminated media is placed and (III) cathode compartment (Fig. 1). EDR has been successfully tried out before in the remediation of different type of fly ashes [10–13].

In the present study we present some of the most successful EDR experiments obtained with different experimental conditions in the remediation of different types of fly ashes: straw (ST) ashes, municipal solid waste (MSW) ashes and co-combustion of wood (CW) ashes. A statistical methodology was applied in order to determine the influence of a given variable on the migration of Ca, Cd, Cr, Cu, Pb and Zn. The biregressional methodology was first developed by Mexia [14] and previously applied in the study of heavy metal migration during EDR on the remediation of soil [15] and timber waste [16,17]. These have been based on simple linear regressions. The methodology is very powerful when migration processes are concerned since it evaluates the effect of each variable on a given metal velocity and acceleration. The novelty of the biregressional design in this study is its application to a categorical dataset.

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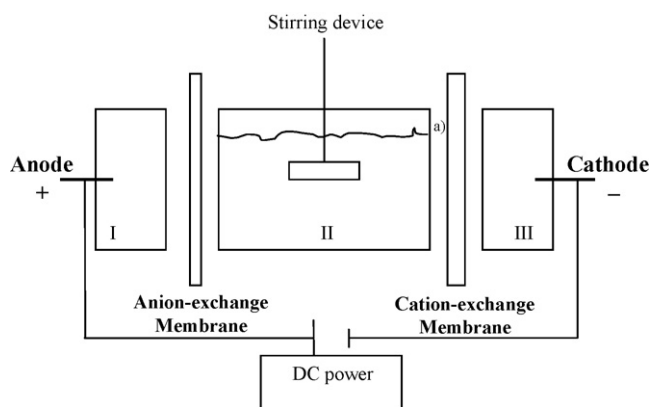


Fig. 1. Setup design for the studied electrochemical experiments. I—anode compartment; II—central compartment; III—cathode compartment; (a) suspension volume level in the electrochemical cell (Pedersen [29]).

2. Materials and methods

2.1. Fly ash sampling

Fly ash samples were collected from different incinerator facilities:

- **DK:** Danish MSW incinerator, Vestforbraending.
- **PT:** Portuguese MSWI, ValorSul.
- **ST:** Danish bio-ash from straw combustion, Avedøre unit 2.
- **CW:** Danish ash from co-combustion of wood and oil, Avedøre unit 2.

Vestforbraending and ValorSul are both incinerators that use MSW as fuel. Combined Heat and Power (CHP) plant Avedøre unit 2 is a cogeneration plant flaming natural gas, fuel oil, straw or a combination of wood and oil as fuels. In CHP plant Avedøre unit 2 each fuel is combusted separately and parameters optimized for maximum efficiency [18].

2.2. Experimental methods

Fly ashes were dried for 24 h at 105 °C and water content was determined. Subsequently, $\text{pH}_{\text{H}_2\text{O}}$ measurements were carried out by suspending 2.5 g the dried fly ash in 12.5 mL distilled water for 1 h and pH was measured by a combined Radiometer pH electrode. The content of Ca, Cd, Cr, Cu, Pb and Zn was quantified by FAAS (atomic absorption spectrophotometry in flame) or graphite furnace, after microwave assisted pressurized digestion of ash: 0.25 g dry ash sample in 10 mL concentrated HNO_3 . Chloride content was measured in H_2O extractions (L/S proportion of 2.5) by Dionex ion chromatograf, DX120.

The electrochemical cell used in this investigation is schematized on Fig. 1 and consisted of three compartment cell, two electrode compartments and central compartment, where the contaminated media was placed. The cell was made from Plexiglas, where the internal diameter was 8 cm and central compartment length was 10 cm. Electrode compartments were separated from central compartment by anion-exchange membrane 204 SZRA B02249C and cation-exchange membrane CR67HUYN12116B, from ionics. Platinum coated electrodes from Permascand were used as working electrodes and a power supply (Hewlett Packard E3612A) maintained a constant current of 40 mA.

Placed on central compartment, the ash suspension was stirred by a flexible plastic flab, with about 5 cm and 6 mm width, fastened to an insulated wire powered by a “Heto” motor with a rotation velocity of 1300 rpm.

Eight electrochemical experiments were carried out. Table 2 resumes the experimental conditions. All experiments were performed with distilled water in a liquid/solid ratio of 4.

In all experiments $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ was used as catholyte. 500 mL of this solution was used as catholyte. Experiments 1–7 were acidified, i.e. catholyte pH was controlled to 2. For this, pH was controlled once a day in the catholyte by adding 0.01 M HNO_3 . As for the anolyte, experiments 1–6 and 8 used 500 mL of $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$. pH was not controlled in the anolyte. Exceptions are given below:

- Experiment 7 used 0.25 mol L^{-1} ammonium citrate in 1.25% ammonia as assisting agent and as anolyte. No control of pH was performed to the anolyte.
- Experiment 8 electrolytes were not acidified. This means that catholyte’s pH was maintained high. As for the anolyte, pH was adjusted to 7 with calcium oxide (solid).

At the end of the experiments the electrodes and membranes were rinsed in $5 \text{ mol L}^{-1} \text{ HNO}_3$ and $1 \text{ mol L}^{-1} \text{ HNO}_3$, respectively, and the concentration of Ca, Cd, Cr, Cu, Pb and Zn were determined by AAS (atomic absorption spectrophotometry) in flame.

2.3. Definition of variables

Eight electrochemical experiments were carried out with varying conditions. The considered variables were the following:

- “Ash type”—ST, CW, PT, DK, nominal variable;
- “Duration”—Remediation time (10, 11 and 14 days), ordinal variable;
- “Initial pH”—Initial pH of the ash, prior to EDR treatment, numerical variable;
- “Final pH”—pH obtained in the ash after EDR treatment, numerical variable;
- “Acidification”—Use, or absence, of acidic conditions during EDR, nominal variable;
- “Dissolution”—Ash dissolution occurring during EDR, related to initial dry weight (%), numerical variable.

In order to model the data, SPSS program was used [19]. Data of total concentrations (initial and final) in fly ash and electrolytes concentration along experimental time represent the information used inputted to SPSS program. The development of this study followed the methodology applied in [16,17].

3. Preliminary analysis

Ratios between final and initial concentrations were used to determine which variables had the higher level of significance on the EDR: “Ash type”; “Duration”; “Initial pH”; “Final pH”; “Acidification”; “Dissolution”; “Metal”. An analysis of variance (ANOVA) was carried out to identify which ordinal or nominal variables presented significant differences between levels (Table 3). This was followed by Bonferroni multiple comparison method, in order to determine differences between levels of the same significant variable (Table 4). To identify the overall significance of the variables on the removal rates, linear (results not presented) and categorical regression (CATREG) (Table 5) were carried out.

An ANOVA was performed to indicate significant differences between levels of nominal or ordinal variables (Table 3). Numerical variables were not considered for ANOVA. “Ash type” and “Acidification” appear to have significant differences among their different levels. Since “Acidification” was a binary variable, it was pointless to perform a multiple comparison test. Bonferroni multiple comparison method was then applied to “Ash type” (Table 4).

In sequence, an overall analysis was carried out to determine which variables had the most influence on EDR efficiencies. A linear regression and a categorical regression (CATREG) were adjusted to the final/initial ratios. Methodologies were compared and CATREG was chosen since variables were categorical (measured at an ordinal or nominal level) and a higher determination coefficient (R^2). Furthermore, CATREG should be used when the relationship between the predictors and the response is expected to be nonlinear. The CATREG model fits the classical linear regression model with nonlinear transformations of the variables, written as

$$\varphi_r(\mathbf{y}) = \sum_{j=1}^J \beta_j \varphi_j(\mathbf{x}_j) + \mathbf{e}, \quad (1)$$

by minimizing the least squares lost function

$$L(\varphi_r; \varphi_1, \dots, \varphi_j; \beta_1, \dots, \beta_j) = N^{-1} \left\| \varphi_r(\mathbf{y}) - \sum_{j=1}^J \beta_j \varphi_j(\mathbf{x}_j) \right\|^2, \quad (2)$$

with N the number of observations, J the number of predictor variables, $\{\beta_j\}, j=1, \dots, J$, the regression coefficients, $\varphi_r(\mathbf{y})$ the transformation for the response variable \mathbf{y} , $\varphi_j(\mathbf{x}_j)$ the transformations for predictor variables $\{\mathbf{x}_j\}, j=1, \dots, J$, and \mathbf{e} the error vector, and where $\|\cdot\|^2$ denotes the squared Euclidean norm. The loss function (2) is minimized over $\{\beta_j\}, \{\varphi_j(\mathbf{x}_j)\}$ and $\varphi_r(\mathbf{y})$ to maximize the least squares fit between $\varphi_r(\mathbf{y})$ and the linear combination $\sum_{j=1}^J \beta_j \varphi_j(\mathbf{x}_j)$. Because the transformed variables $\varphi_r(\mathbf{y})$ and $\varphi_j(\mathbf{x}_j)$ are centered and normalized to have sum of squares equal to N , loss function (2) maximizes the (squared) multiple correlation [20]. The results from CATREG are shown in Table 5.

3.1. Results and discussion

Table 1 summarizes the major characteristics of the studied fly ashes. Descriptions and thorough characterization of these ashes can be found in Lima et al. [13,18].

Table 1

General characteristics of DK, PT, ST and CW fly ash (adapted from Lima et al. [18]).

Parameter	DK	PT	ST	CW
Fuel	MSW	MSW	Straw	Wood and oil
pH	12.2 ± 0.01	11.9 ± 0.01	5.9 ± 0.04	12.0 ± 0.2
Water content (%)	1.28	1.05	1.16	0.40
Cl content (%) ^a	21.50	9.81	21.14	0.34
Ca content (%)	14	22.2	0.76–0.86	8.73
Cr (mg kg ⁻¹) ^b	284.7 ± 3.2	184.8 ± 5.9	13.54 ± 0.43	185.0 ± 1.3
Cd (mg kg ⁻¹) ^b	240.6 ± 18.2	83.4 ± 0.8	11.3 ± 0.01	22.36 ± 0.06
Cu (mg kg ⁻¹)	2206 ± 70	586 ± 7.8	80.5 ± 1.1	232.9 ± 0.03
Zn (mg kg ⁻¹)	26,958 ± 710	4900 ± 34	305.7 ± 0.09	2015 ± 1.4
Pb (mg kg ⁻¹)	8507 ± 42	2462 ± 71	17.3 ± 0.87	1224 ± 0.03

^a Water soluble (L/S ratio = 2.5).

^b In [14].

Table 2 presents the ratios between the final and initial concentration of metals. Final concentration signifies the concentration of metals in the ashes obtained after experiments. Thus, ratios closer to zero corresponds to the most successful experiments. Regarding the best removal rates – on italic in Table 2 – experiment 8 was considered the most successful based on direct observation. It is also worth mentioning that this experiment lasted 11 days, where the final ash retained a high pH and undergone low ash dissolution. This is a good indication that CW ash would still be valuable for reuse, e.g. in concrete or ceramics, after remediated through EDR.

An ANOVA was carried out to determine which variables presented significant differences between levels. “Ash type” presented significant differences (Table 3) and was then considered for Bonferroni multiple comparison test in order to determine which levels have significant differences. Table 4 shows ST and CW ash as being significantly different in terms of the EDR efficiency (p -value = 0.016). The higher the amplitude (negative) given by (I - J) was, the lower the final/initial ratios. This implies a positive influence of EDR on the metals removal rates since the lower the ratio, the higher the metal removal. Therefore, CW ash treatment was

Table 2

Resume of ashes parameters after experimental time and final/initial concentration ratios.

Experiment	Ash type	Duration (days)	Final pH	Acidification	Dissolution	Cd ratio	Cr ratio	Ca ratio	Cu ratio	Zn ratio	Pb ratio
1	ST	10	1.9	Yes	95.5	1.21	2.98	1.05	1.70	1.33	1.09
2	ST	14	2.1	Yes	95.2	0.37	4.14	0.95	0.71	1.29	0.93
3	CW	10	9.9	Yes	20.6	1.94	0.42	0.54	0.63	0.57	1.06
4	CW	14	7.0	Yes	29.0	0.89	0.63	0.50	0.61	0.52	0.88
5	PT	14	7.9	Yes	71.9	1.15	1.66	1.02	1.68	1.35	1.26
6	DK	14	7.3	Yes	55.7	1.16	1.61	0.98	1.95	0.91	1.78
7	PT	14	9.0	No	12.8	0.33	0.76	0.69	0.46	0.71	0.80
8	CW	11	11.8	No	17.2	0.18	0.63	0.55	0.52	0.61	0.53

Italic—best removals from direct observation.

Table 3

ANOVA test for determining the significance difference between levels of a variable in the final/initial ratio.

	Sum of squares	df	Mean square	F	p-value
Between “Ash Type” groups	5.461	3	1.820	4.548	0.007
Within “Ash Type” groups	17.612	44	0.400		
Total	23.072	47			
Between “Acidification” groups	3.694	1	3.694	8.768	0.005
Within “Acidification” groups	19.379	46	0.421		
Total	23.072	47			
Between “Duration” groups	2.141	2	1.071	2.302	0.112
Within “Duration” groups	20.931	45	0.465		
Total	23.072	47			
Between “Metals” groups	3.355	5	0.671	1.429	0.234
Within “Metals” groups	19.718	42	0.469		
Total	23.071	47			

Bold—significant, p-value inferior to 0.05.

Table 4

Multiple comparisons test using Bonferroni method, with final/initial ratios as dependent variable, for “Ash type”.

(I) Ash type	(J) Ash type	Mean difference (I–J)	Std. error	p-value	95% confidence interval	
					Lower bound	Upper bound
ST	CW	0.80102*	0.23578	0.016	0.1157	1.4864
	DK	0.08267	0.31633	0.995	–0.8368	1.0022
	PT	0.80102	0.25828	0.324	–0.2626	1.2389
CW	ST	–0.80102*	0.23578	0.016	–1.4864	–0.1157
	DK	–0.71835	0.29824	0.138	–1.5853	0.1486
	PT	–0.31287	0.23578	0.627	–0.9982	0.3725
DK	ST	–0.08267	0.31633	0.995	–1.0022	0.8368
	CW	0.71835	0.29824	0.138	–0.1486	1.5853
	PT	0.40548	0.31633	0.652	–0.5140	1.3250
PT	ST	–0.48815	0.25828	0.324	–1.2389	0.2626
	CW	0.31287	0.23578	0.627	–0.3725	0.9982
	DK	–0.40548	0.31633	0.652	–1.3250	0.5140

Bold—significantly different, p-value inferior to 0.05.

Italic—high similarity, p-value close to 1.

* The mean difference is significant at the 0.05 level.

considered more successful than ST ash (Table 4), also in accordance with observations in Table 2. According to Lima et al. [13], the CW ashes successful remediation in an acidic media could be mainly due to the removal of Ca, and possibly Zn, during the EDR, since the removal of the target heavy metals, e.g. Cd, Cr, Cu, Pb from CW ash could be neglected (experiments 3 and 4 in this paper). Plus, ST ashes remediation showed high similarities (p -value = 0.995) with DK ashes (Table 4). According to Table 2, ST ashes presented the highest ratios, i.e. lowest removal of metals. The parameters used to regulate ST and DK ashes remediation may not be the most suitable for the removal of the target metals.

Discretization was applied in order to obtain Table 5. CATREG determined that “Ash type”, “Duration”, “Dissolution” and “Metal” were the most significant on Ca, Cd, Cr, Cu, Pb and Zn ratios. The positive or negative value of the variable coefficient (Beta) in Table 5 has a physical interpretation. “Duration” was highly significant on EDR, where Beta < 0 indicates that an increasing experimental time provides lower metal ratios, i.e. longer remediation periods translate in higher removal efficiencies, since a low final/initial concentration ratio indicates high removal. According to several studies regarding EDR application to a porous media, e.g. [21–23], consensus is found on using longer remediation periods to achieve higher removal efficiencies. Regarding “dissolution”, augmenting the dissolution of the ashes during EDR incites higher metal ratios in Table 2, i.e. lower removal efficiencies. For instance, MSW ashes dissolution was expected to be lower when compared with straw or wood ashes, even though alkali based salts may be observed in their matrix [18,24]. MSW ashes have in fact large amounts of the Cl[–], due to condensation of salts on fly ash particles surface in the flue gas [25]. Although this is true, the potassium content is still higher in straw ashes [18,26], making them more likely to dissolve.

Table 5

Categorical regression and respective standardized regression coefficients for the interaction between the variables and final/initial ratio.

	Standardized coefficients		df	F	p-value
	Beta	Std. error			
Ash type	0.444	0.187	3	5.622	0.003
Duration	–0.334	0.166	1	4.066	0.052
Initial pH	0.338	0.200	1	2.876	0.100
Final pH	–0.232	0.400	1	0.337	0.566
Acidification	–0.187	0.190	1	0.963	0.334
Dissolution	0.708	0.291	4	5.919	0.001
Metal	0.185	0.106	5	3.028	0.024

Bold—significant, with significance level inferior to 0.05.

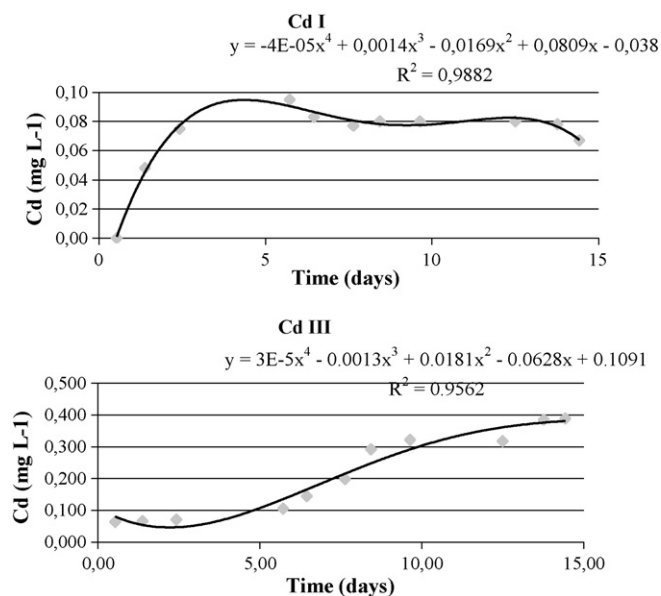
* R² of 0.649; p-value of correspondent ANOVA of 0.001.

Finally, the remaining significant variables in Table 5, “Ash type” and “Metal”, were not possible to interpret due to their nominal scale. Metal could in fact explain the studied ratios (p -value = 0.024 in Table 5) but according to Table 3, the variable “Metal” showed no statistical difference between the different levels (p -value = 0.234), which means that metals are removed independently during EDR. Resuming, the ratios differ significantly from metal to metal. This also makes sense since metals are expected to have different ionic mobility once subjected to an electric field [27].

4. Nonlinear biregressional study

The main goal of EDR is to remove the heavy metals present in a contaminated material, placed in compartment II. In a general sense, electric current drags the electrically charged elements according to their charge into one of the electrode compartments, I and III. The migration of the metals was controlled and quantified along remediation time.

In order to understand heavy metals migration rate, and to carry out inference on the studied variables, a biregressional methodol-

**Fig. 2.** Cd concentration evolution along experimental time in AN and CAT during EDR for experiment 1.

ogy was preformed. First, a 4th degree polynomial regression was adjusted to each compartment I (AN) and compartment III (CAT) heavy metal concentration, which varied along time. Fig. 2 shows one example of Cd concentration profile along time in compartment I (AN) and compartment III (CAT) (in experiment 1) with 4th degree polynomials adjusted:

$$y_i(t) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + e_i; \quad i = 1, \dots, n,$$

where $e_i \sim N(0, \sigma^2)$ and n the number of experiments. In matrix notation the previous equation becomes

$$\begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} 1 & t_1 & t_1^2 & t_1^3 & t_1^4 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & t_n & t_n^2 & t_n^3 & t_n^4 \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} + \begin{bmatrix} e_1 \\ e_2 \\ \vdots \\ e_n \end{bmatrix}$$

or $\mathbf{y} = \mathbf{T}\mathbf{a} + \mathbf{e}$, with $E(\mathbf{e}) = \mathbf{0}$ and $\text{Cov}(\mathbf{e}) = E(\mathbf{e}\mathbf{e}') = \sigma^2\mathbf{I}$.

To complete the analysis, a second series of regression were adjusted to each $a_j, j=0, \dots, 4$ using the selected “Ash type”, “Duration”, “Final pH” and “Dissolution” as explanatory variables. However, since some variables are non numerical, a categorical regression (CATREG) was applied instead of the linear used in Moreira et al. [17], where the model matrix \mathbf{T} for this regression had the column vectors associated to the factors (variables) [14,16]. This generalization resulted in the denominated nonlinear biregression analysis.

The parameters a_0, a_1, \dots, a_4 of this first series of regressions were obtained and the first three parameters of the polynomial were chosen due to their physical significance:

a_0 —estimates the initial concentration at the beginning of the time series;

a_1 —measures the initial rate of migration, i.e. the velocity that the metal is entering the electrolyte compartments;

a_2 —measures the initial acceleration (Beta > 0) or deceleration (Beta < 0) of the migration, i.e. the rate that one object/metal changes its migration velocity.

a_0, a_1 and a_2 are then the kinetic parameters for metals migration during EDR. A second series of regressions using CATREG was then carried out, where the dependent variables were the adjusted coefficients of the first set of regressions (this table was omitted) and the independent variables the levels of “Ash type”, “Duration”, “Final pH” and “Dissolution”. The results are presented in Table 6. The regressions used were categorical, since discretization of the variables was still needed. Since there were missing values, the option “Mode” for the CATREG procedure was used in order to input them [19].

Considering a significance level of 5%, it was seen that all studied variables inferred statistically on Cd and Cu migration to compartment III, but not on the remaining metals. This is in accordance with previous studies [10,11,28,29], where Cd and Cu were mainly found as cations in fly ashes and easily transported towards the cathode.

The Cd III results in Table 6 can be interpreted as following: the lower the “Final pH”, the more reliable initial concentration (a_0) on compartment III (Beta < 0), i.e. no need for correction factor; the higher the migration velocity (a_1) (Beta > 0); the lower the rate of variation of velocity (a_2) (Beta < 0). This interpretation is valid for any variable with p -value < 0.05, with Beta as a positive or negative value.

“Ash type” was also found to influence a_0 on Ca and Pb concentrations of compartment III. Furthermore, if considering p -value < 0.10, “Ash type” influences all studied initial concentration of metals (a_0), in compartment I or III, depending on the metal. This indicates that, depending on the remediated ash,

Table 6 CATREG between each a_0, a_1, a_2 of the previous set of regressions on Cd, Cu, Pb and Zn in each compartment I and compartment III anode and cathode compartments, and each considered variable (e.g. “Ash type”).

		Cd I		Cd III		Cr I		Cr III		Ca I		Ca III		Cu I		Cu III		Zn I		Zn III		Pb I		Pb III	
		Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value	Beta	p-value
a_0	Ash type	0.74	0.80	1.02	0.01	1.11	0.07	1.21	0.23	1.20	0.09	1.06	0.03	0.90	0.46	1.17	0.01	1.04	0.06	1.19	0.09	-0.92	0.49	-0.99	0.01
	Duration	-0.55	0.54	-0.33	0.02	0.06	0.66	-0.53	0.37	0.15	0.44	-0.15	0.17	-0.49	0.55	-0.01	0.53	-0.03	0.74	0.15	0.45	0.49	0.56	0.01	0.56
	Final pH	1.41	0.58	-2.24	0.01	-0.45	0.33	-0.18	0.86	-0.77	0.24	-0.17	0.32	-0.21	0.91	-0.83	0.01	-0.24	0.40	-0.79	0.24	-1.06	0.56	0.01	0.38
	Dissolution	1.66	0.48	-1.46	0.01	-1.14	0.14	0.32	0.73	-1.95	0.10	0.13	0.40	-0.26	0.89	-1.99	0.01	-0.47	0.22	-1.95	0.10	-0.62	0.73	0.01	0.64
R^2		0.674		1.000		0.992		0.936		0.987		0.999		0.741		1.000		0.996		0.987		0.987		0.770	1.000
a_1	Ash type	-0.92	0.40	-0.63	0.01	-1.19	0.25	-1.19	0.25	0.34	0.18	1.05	0.05	0.73	0.38	-1.58	0.00	-1.95	0.43	-1.84	0.27	-0.86	0.07	-0.89	0.36
	Duration	0.59	0.45	-0.34	0.01	0.32	0.46	0.32	0.46	-0.10	0.45	0.06	0.60	0.32	0.46	-0.15	0.02	-0.46	0.59	0.09	0.84	0.08	0.48	-0.26	0.45
	Final pH	0.07	0.97	1.81	0.01	2.35	0.20	2.36	0.21	0.53	0.25	-0.41	0.30	-1.66	0.28	-1.29	0.01	-1.58	0.52	-1.16	0.46	0.75	0.15	0.04	0.96
	Dissolution	-0.04	0.98	1.86	0.01	1.04	0.37	1.04	0.37	1.35	0.10	-1.02	0.13	-0.39	0.67	0.81	0.01	0.64	0.69	0.67	0.59	0.35	0.31	0.10	0.86
R^2		0.795		0.938		0.938		0.994		0.994		0.994		0.784		1.000		0.784		0.895		0.895		0.996	0.971
a_2	Ash type	0.81	0.362	-2.09	0.00	1.75	0.34	-0.79	0.25	1.30	0.21	1.19	0.18	1.03	0.39	1.23	0.00	1.76	0.33	1.08	0.44	-1.50	0.68	-0.93	0.72
	Duration	0.25	0.467	-0.21	0.01	0.26	0.65	0.55	0.18	-0.17	0.67	-0.65	0.25	0.23	0.54	-0.23	0.02	0.23	0.69	-0.45	0.61	0.55	0.72	0.59	0.67
	Final pH	-2.78	0.148	-1.24	0.01	-1.86	0.38	0.05	0.94	-0.91	0.41	-0.71	0.46	-2.34	0.19	-0.65	0.02	-1.80	0.39	-1.76	0.42	1.25	0.73	-0.10	0.97
	Dissolution	-2.30	0.146	0.79	0.01	-0.34	0.80	-1.28	0.20	-1.78	0.25	0.30	0.69	-1.82	0.19	-0.79	0.01	-0.23	0.87	-2.01	0.40	0.21	0.93	-0.33	0.90
R^2		0.960		0.851		0.977		0.935		0.935		0.955		0.952		1.000		0.837		0.748		0.475		0.535	0.851

Bold—significant values with $\alpha < 0.05$; italic—significant values with $\alpha < 0.10$.

initial concentration in the electrolytes requires an adjustment factor.

a_1 , or migration velocity, may be the most significant physical parameter to interpret from this analysis. Cd and Cu migrate preferably towards the cathode, and with exception of “Final pH”, the interpretation is the same for both metals. The metals velocity towards the cathode increase significantly:

- with decreasing “Duration” or experimental time;
- with increasing ash “Dissolution” during EDR.

Regarding “Final pH”, Cd seems to be faster with higher final pH, while Cu seems to increase in velocity migration with lower final pH.

5. Resume

“Ash type”, “Duration” and “Dissolution” were considered the variables with most significance on heavy metal migration during electrochemical experiments. Increasing remediation time proportionate higher removal efficiencies, while increasing the dissolution of the ash during EDR translates in lower removal efficiencies. CW and ST ash were considered significantly different by Bonferroni multiple comparison test, and overall, the “ash type” was considered a significant variable to EDR.

The birregressional study was found to be a useful tool when there is a need of physical interpretation of the results, especially initial concentration and velocity migration. All the considered variables, “Ash type”, “Duration”, “Final pH” and “Dissolution”, were found to significantly influence Cd and Cu migration towards the cathode. Overall, the birregressional study outlines Cd and Cu migration towards the cathode, indicating that the used experimental conditions influence greatly the migration velocity of these two heavy metals. As for the remaining metals, further experiments are necessary to understand which type of variables influence their migration to the electrode compartments.

Acknowledgement

A.T. Lima acknowledges her PhD. supervisors A.B. Ribeiro and L.M. Ottosen for their support.

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