

Modelling the effect of different conditions on electroremediation of fly ash from a municipal solid waste incinerator

**A.T. Lima^{1*}, M. Fonseca², A.B. Ribeiro¹, J.T. Mexia²,
A. Varela-Castro³, L. Ottosen⁴**

¹ Department of Science and Environmental Engineering, Faculty of Science and Technology,
Nova University of Lisbon, 2829-516 Caparica, Portugal

² Department of Mathematics, Faculty of Science and Technology, Nova University of Lisbon,
2829-516 Caparica, Portugal

³ National Agronomical Station, Department of Soil Science, Av. República, 2784-505
Oeiras, Portugal

⁴ Civil Engineering Department, Brovej, Building 118, Technical University of Denmark,
DK-2800 Lyngby, Denmark

SUMMARY

Fly ashes from Municipal Solid Waste Incinerators (MSWI) are considered hazardous waste where current practice is to deposit them in landfill. The Electrodialytic Process (EDR) is a remediation technique, which was first applied in contaminated soil remediation. The principle combines electric current with dialysis and aims to remove heavy metals from contaminated solid media. In the present study, an eighteen electro-dialytic experiment batch was carried out with different combinations of variables with presumed influence on EDR. Variables such as "Ash %", "Current", "Duration", "Length" and "Metal" were considered. The level of significance of each variable for general EDR performance was determined by F tests and Scheffé's multiple comparison method. It was possible to build up a gradated sequence for the variables "Current" and "Ash %". For a general analysis, linear regressions and F tests were carried out individually for each variable to study its influence on the removal of each studied metal (Fe, Mn, Cu, Zn, Cd, Cr, Pb and Ni). "Length" was found to be the variable with the most effect on EDR efficiency, followed by "Ash %". Furthermore a multiple regression design approach was used to evaluate EDR performance throughout the remediation time. It might be concluded that a given variable affects the removal of the metal by positive or negative species.

Key words: Electrodialytic Process, F tests, Fly ash, Multiple regression design, Scheffé multiple test

1. Introduction

Incineration of household and industrial residues is current practice in many European countries. The outputs of this process can be environmentally unsafe since all the volatile elements, e.g. heavy metals, can be found in this fraction. Municipal Solid Waste Incinerator (MSWI) fly ashes are considered hazardous waste according to EU Commission Directive 2000/532/CE, dated 3 May 2000. Due to their hazardous nature, fly ashes are inertized before their disposal in landfill. This procedure represents a waste of raw material, energy and landfill area, posing a growing environmental management concern. Nevertheless, fly ash is rich in two major nutrients, phosphorus and potassium, and therefore has some potential to be used as raw material (Ferreira et al., 2003). Fly ash from MSWIs may still be a valuable resource, in different industrial sectors, if its hazardous components could be removed.

The electrodiolytic (EDR) process is a remediation technique, with verified success, that has been applied to several matrices since it was first described for heavy metal contaminated soil (Hansen et al., 1997; Ottosen et al., 1997; Ottosen and Hansen, 1992). The method has been tested for contaminated soil (Ribeiro, 1998), harbour sludge (Nistroem et al., 2005), impregnated waste wood (Ribeiro et al., 2000) and different ash residues (Pedersen, 2003). It consists in a flux of ions and water from one electric pole to the other. This method comprises the principles of electrokinetics and electrodialysis, i.e. a combination of electric current as the cleaning agent with ion-exchange membranes that allow regulation of ion fluxes. The ability to transform sorbed heavy metals into ionic forms or more mobile complexes in solution is EDR's main goal. During experiment, the cathode compartment receives positive species (among them positive trace metal complexes) that are able to migrate through the porous media and pass the cation-exchange membrane. The anode compartment receives negative species/complexes that are able to pass the anion-exchange membrane.

This paper aims to introduce a new statistical methodology for the understanding of heavy metals' behaviour during the EDR process. A biregressional approach has been developed by Mexia (1990) and applied previously in the study of heavy metal migration in EDR soil remediation (Ribeiro and Mexia, 1997) and timber waste (Moreira et al, 2005a; Moreira et al., 2005b). The purpose of this study is to analyse the influence of different experimental conditions, for EDR fly ash remediation, in order to optimize the process and obtain the highest efficiency possible in the removal of heavy metals.

2. Experimental Section

2.1. Experimental Setup

The electrodialytic cell used in this study followed the principle presented in Figure 1 which is based on a concept developed at the Technical University of Denmark (Ottosen and Hansen, 1992). Compartment II contained fly ash blended with an assisting agent, which consisted of 0.25M ammonium citrate in 1.25% NH_3 . Compartments I and II were separated by an anion-exchange membrane (IA1-204SXZL386). The anolyte used in recirculation in Compartment I was 0.25M ammonium citrate in 1.25% NH_3 . Between compartments II and III there was a cation-exchange membrane (IC1-61CZL386). In compartment III, 10^{-2}M NaNO_3 circulated as catholyte. The catholyte was periodically adjusted to pH ~ 2 by addition of concentrated HNO_3 .

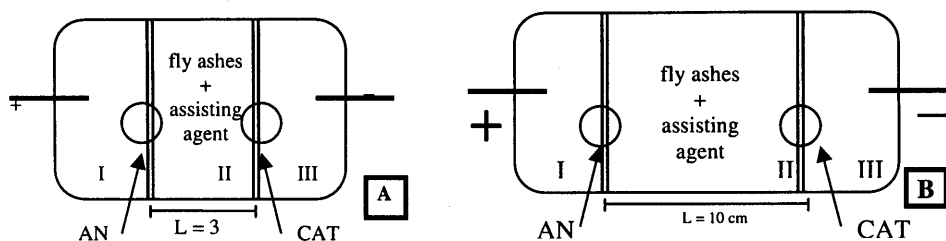


Figure 1. Experimental setup design. AN – anion exchange membrane; CAT – cation exchange membrane; I – anode compartment; II – central compartment; III – cathode compartment.

Both ion-exchange membranes IC1-61CZL386 and IA1-204SXZL386 were supplied by Ionics Inc., USA. A power supply unit (Hewlett-Packard E3612A) was used to pass current (DC) between working platinum-coated electrodes (Bergsoe AC, Denmark). The initial anolyte and catholyte solutions were the same in all experiments, as was the assisting agent.

Total concentrations of Fe, Mn, Cu, Zn, Cd, Cr, Pb and Ni in fly ash were determined for initial fly ash and after the EDR experiments using an aqua-regia procedure (HNO_3/HCl). The liquid-to-solid (L/S) ratio used in the digestion was 25 and afterwards the samples were vacuum filtered through a $0.45\ \mu\text{m}$ filter. Series of two replicates were carried out and concentration of Fe, Mn, Cu, Zn, Cd, Cr, Pb and Ni analysed in an Atomic Absorption Spectrophotometer. Furthermore, concentrations of Cd, Cu, Pb and Zn were determined in the electrolytes by Atomic Absorption Spectrophotometry.

2.2. Definition of Variables of the ED process

Eighteen electrodialytic experiments were carried out with varying conditions. A sequential list of the considered variables is given:

“Length” – Central compartment length (3 and 10 cm)

“Duration” – Remediation time (14 and 21 days)

“Current” – Applied current (0, 20, 40, 60 and 80mA)

“Ash %” – Ash percentage (50, 75, 90 and 100%)

“Metal” – Studied metal (Fe, Mn, Cu, Zn, Cd, Cr, Pb and Ni)

2.3. Analytical Methods

In order to model the data, the SPSS program was used (SPSS INC., 1989). Data on total concentrations (initial and final) in fly ash and electrolytes concentration over experimental time represent the information input to the SPSS program. The development of this study followed the methodology applied in (Moreira et al, 2005a; Moreira et al., 2005b).

3. Results and Discussion

The F test and Scheffé’s multiple comparison method were used to assess the significance level of the variables in Table 1 and to choose the most significant experiments for further developments (see section 3.1.).

In the selected experiments, a multiple regression (biregessional) design approach was taken to study the metals’ behaviour over experimental time (see section 3.2.).

Table 1. Description of the experiments, listing the factor levels

Experiment	Ash %	Current (mA)	Duration (days)	Length (cm)
1	75	40	21	10
2	90	40	21	10
3	100	40	21	10
4	50	40	14	10
5	75	40	14	10
6	90	40	14	10
7	100	40	14	10
8	50	40	21	10
9	100	0	14	10
10	50	40	14	3
11	100	40	14	3
12	90	40	14	3

13	65	40	14	3
14	75	20	14	3
15	75	60	14	3
16	75	80	14	3
17	75	0	14	3
18	100	0	14	3

3.1 Analysis of Concentration Ratios

In this section, ratios between final and initial concentrations were analysed in order to determine the variables with the most significant effect on EDR (“Ash %”; “Current”; “Duration”; “Length”; “Metal”). The data was analysed using F tests and Scheffé’s multiple comparison method.

The F tests and their p-values are presented in Table 2. It may be concluded that “Current”, “Ash %”, “Length” and “Metal” are highly significant variables for EDR efficiency, while “Duration” had no significance for the process.

Table 2. F test for all variables using concentration ratios (adopted from SPSS INC. 1989)

Source	Type III Sum of Squares	df	Mean Square	F	p-value	Noncent. Parameter	Observed Power(a)
Corrected Model	6.265(b)	17	.369	13.231	.000	224.922	1.000
Intercept	11.279	1	11.279	404.919	.000	404.919	1.000
Current	1.320	4	.330	11.849	.000	47.396	1.000
Ash %	1.163	4	.291	10.436	.000	41.745	1.000
Duration	.000	1	.000	.014	.907	.014	.052
Length	1.121	1	1.121	40.244	.000	40.244	1.000
Metal	2.208	7	.315	11.323	.000	79.260	1.000
Error	3.398	122	.028				
Total	84.224	140					
Corrected Total	9.663	139					

Bold – Significant values with $\alpha < 0.05$

Scheffé’s multiple comparison method was used to compare the removal efficiencies at different levels of “Current” and “Ash %” (Table 3 and 4). These were the variables found to be significant, and hence more than two levels were considered.

Table 3. Multiple Comparisons Test using Scheffé method, with concentration ratios, for “Current” (adopted from SPSS INC. 1989)

(I) Current	(J) Current	Mean Difference (I-J)	Std. Error	p-value	95% Confidence Interval	
					Lower Bound	Upper Bound
0.00	20.00	-.2227	.07204	.055	-.4481	.0026
	40.00	-.2234	.03878	.000	-.3447	-.1021
	60.00	-.1474	.06850	.333	-.3617	.0669
	80.00	.1999	.07204	.110	-.0254	.4253
20.00	0.00	.2227	.07204	.055	-.0026	.4481
	40.00	-.0007	.06536	1.000	-.2052	.2038
	60.00	.0753	.08638	.943	-.1948	.3455
	80.00	.4226	.08921	.000	.1436	.7017
40.00	0.00	.2234	.03878	.000	.1021	.3447
	20.00	.0007	.06536	1.000	-.2038	.2052
	60.00	.0760	.06144	.821	-.1161	.2682
	80.00	.4233	.06536	.000	.2189	.6278
60.00	0.00	.1474	.06850	.333	-.0669	.3617
	20.00	-.0753	.08638	.943	-.3455	.1948
	40.00	-.0760	.06144	.821	-.2682	.1161
	80.00	.3473	.08638	.004	.0771	.6175
80.00	0.00	-.1999	.07204	.110	-.4253	.0254
	20.00	-.4226	.08921	.000	-.7017	-.1436
	40.00	-.4233	.06536	.000	-.6278	-.2189
	60.00	-.3473	.08638	.004	-.6175	-.0771

Bold – Significant values with $\alpha < 0.05$

Table 4. Multiple Comparisons Test using Scheffé method, with concentration ratios, for “Ash %” (adopted from SPSS INC. 1989)

(I) Ash	(J) Ash	Mean Difference (I-J)	Std. Error	p-value	95% Confidence Interval	
					Lower Bound	Upper Bound
50.00	65.00	-.2256	.06850	.033	-.4399	-.0113
	75.00	.0381	.04278	.939	-.0957	.1719
	90.00	-.0747	.04870	.672	-.2270	.0776
	100.00	-.0933	.04367	.341	-.2299	.0433
65.00	50.00	.2256	.06850	.033	.0113	.4399
	75.00	.2637	.06404	.003	.0634	.4640
	90.00	.1509	.06814	.303	.0622	.3640
	100.00	.1323	.06464	.386	.0699	.3345
75.00	50.00	-.0381	.04278	.939	-.1719	.0957
	65.00	-.637	.06404	.003	-.4640	-.0634
	90.00	-.1128	.04219	.135	-.2448	.0191
	100.00	-.1314	.03627	.014	-.2449	-.0180

90.00	50.00	.0747	.04870	.672	-.0776	.2270
	65.00	-.1509	.06814	.303	-.3640	.0622
	75.00	.1128	.04219	.135	-.0191	.2448
	100.00	-.0186	.04309	.996	-.1534	.1162
100.00	50.00	.0933	.04367	.341	-.0433	.2299
	65.00	-.1323	.06464	.386	-.3345	.0699
	75.00	.1314	.03627	.014	.0180	.2449
	90.00	.0186	.04309	.996	-.1162	.1534

Bold – Significant values with $\alpha < 0.05$

Table 3 shows that there are no significant differences between applying 20, 40 or 60 and 0 or 80 mA of “Current”. It can also be seen that an applied current of 40mA gives the highest ratio, i.e. the lowest removal efficiency. When a difference with negative amplitude is found in the SPSS Scheffé output it translates into a positive effect on EDR removal efficiency. An applied current of 80mA is therefore the best current for metal removal efficiency. A graded sequence of current is suggested, based on best removal rates: $80\text{mA}^- > 0\text{mA}^- > 60\text{mA}^- > 20\text{mA}^- > 40\text{mA}$. Nevertheless, this outcome does not show coherence with practical results. The variable “Current” will be discussed further in this paper.

Table 4 shows that there are no significant differences between 50, 75 or 90% and 65 or 100% of ash. The suggested sequence of “Ash %” for the most efficient removal by EDR is $75\%^- > 50\%^- > 90\%^- > 100\%^- > 65\%$.

To validate these results, a Kolmogorov-Smirnov test of normality of residues was carried out. The results are presented in Table 5, showing no significant departure from normality.

After a general analysis of the concentration ratios, two linear regressions were adjusted per metal. The controlled variables were “Current”, “Ash %”, “Duration” and “Length”. The SPSS program (SPSS INC., 1989) was used and the regression results are presented in Table 6. The response variables for these regressions were:

$$Y_1 = \text{Final Concentration} / \text{Initial concentration}$$

$$Y_2 = \text{Final Concentration} - \text{Initial concentration}$$

To complete this phase of the analysis, ANOVA was carried out for Y_1 for each metal. The results are presented in Table 7.

Table 5. One-Sample Kolmogorov-Smirnov Test calculated from results used for calculation of table 2 (adopted from SPSS INC. 1989)

		Standardized Residual for ratio
N		14000
Normal Parameters	Mean	0.000
	Std. Deviation	0.93686
Most Extreme Differences	Absolute	0.048
	Positive	0.048
	Negative	-0.034
Kolmogorov-Smirnov Z		0.569
Asymp. Sig. (2-tailed)		0.902

Table 6 shows that “Length” has a positive influence on Y_1 . Consequently, “Length” was the only variable with representative effect on the removal of Cd, Cu, Fe and Mn from the central compartment. When considering Y_2 outputs, the variables presenting some significance level (α) were “Ash %” for the removal of Cr and Ni, “Duration” for removal of Mn and “Length” for Fe and Ni (Table 6). Overall, “Current” presented no level of significance for the removal of the selected metals.

F tests were carried out for each metal (Table 7). At a significance level $\alpha < 0.05$, “Current” affects significantly the EDR removal of Cr, Cu, Pb and Zn; “Ash %” affects significantly the electro dialytic removal of Cu, Pb and Zn; and “Length” affects significantly the electro dialytic removal of Cd, Cu, Pb and Zn. “Duration” was found to have no significant influence on the EDR remediation of MSWI fly ash. It could also be seen that none of the studied variables had significant influence on the EDR removal of Fe, Mn and Ni.

In comparing the results in Table 6 and Table 7, some differences are noted. The resolutions in Table 6 were based on the linear regression assumption, i.e. that all variables assumed a linear pattern, while the F tests allowed each variable to have several levels (Table 7). Since a linear assumption may not be true for our dataset, F tests may be considered more reliable for the analysis.

Table 6. Level of significance of each linear regression on the interaction of variable “Current”/”Ash %”/”Duration”/”Length” on the removal of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn

	Y1 Cd		Y1 Cr		Y1 Cu		Y1 Fe		Y1 Mn		Y1 Ni		Y1 Pb		Y1 Zn	
	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value
Current	-0.26	0.80	0.14	0.89	-0.11	0.91	1.47	0.17	0.54	0.60	0.52	0.61	0.73	0.48	0.43	0.67
Ash %	0.83	0.42	-0.82	0.43	0.46	0.66	2.32	0.04	0.98	0.34	0.49	0.63	1.35	0.20	0.28	0.78
Duration	0.50	0.63	0.12	0.90	-0.21	0.84	-0.12	0.90	1.05	0.32	0.64	0.53	-0.43	0.67	-0.55	0.59
Length	3.97	0.00	1.22	0.25	2.10	0.06	2.28	0.04	2.41	0.03	0.79	0.44	1.16	0.27	1.54	0.15
	Y2 Cd		Y2 Cr		Y2 Cu		Y2 Fe		Y2 Mn		Y2 Ni		Y2 Pb		Y2 Zn	
	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value
Current	0.36	0.72	0.21	0.83	0.49	0.63	1.01	0.33	0.45	0.66	0.19	0.85	0.85	0.41	0.69	0.50
Ash %	-0.29	0.78	-1.97	0.07	0.55	0.59	0.01	0.99	0.17	0.86	-2.65	0.02	1.14	0.28	-0.22	0.83
Duration	0.78	0.45	0.67	0.51	-0.66	0.52	0.02	0.99	2.21	0.05	1.23	0.24	-1.24	0.24	-1.38	0.19
Length	-0.80	0.44	-1.25	0.23	1.11	0.29	-2.74	0.02	0.07	0.95	-5.23	0.00	0.49	0.63	1.17	0.26

Bold – Significant values with $\alpha < 0.05$

Table 7. F tests for each metal Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn using concentration ratios (adopted from SPSS INC. 1989)

Studied Metal	Source	Type III Sum of Squares	df	Mean Square	F	p-value	Noncent. Parameter	Observed Power
Cd	C.Model	1.090(b)	10	.109	6.076	.013	60.757	.910
	Intercept	1.004	1	1.004	55.978	.000	55.978	1.000
	Current	.171	4	.043	2.387	.149	9.547	.407
	Ash %	.151	4	.038	2.108	.183	8.432	.363
	Duration	.007	1	.007	.376	.559	.376	.083
	Length	.508	1	.508	28.302	.001	28.302	.995
	Error	.126	7	.018				
	Total	6.549	18					
	C.Total	1.215	17					
Cr	C.Model	.518(b)	10	.052	3.089	.074	30.889	.619
	Intercept	1.282	1	1.282	76.490	.000	76.490	1.000
	Current	.375	4	.094	5.592	.024	22.369	.785
	Ash %	.045	4	.011	.672	.632	2.687	.138
	Duration	.001	1	.001	.057	.818	.057	.055
	Length	.035	1	.035	2.084	.192	2.084	.240
	Error	.117	7	.017				
	Total	11.448	18					
	C.Total	.635	17					
Cu	C.Model	.800(b)	10	.080	6.555	.010	65.549	.931
	Intercept	1.849	1	1.849	151.561	.000	151.561	1.000
	Current	.247	4	.062	5.070	.031	20.278	.741
	Ash %	.277	4	.069	5.670	.023	22.680	.791
	Duration	.005	1	.005	.382	.556	.382	.084
	Length	.216	1	.216	17.685	.004	17.685	.948
	Error	.085	7	.012				
	Total	13.343	18					
	C.Total	.885	17					
Fe	C.Model	.333(b)	10	.033	1.772	.230	17.720	.375
	Intercept	.570	1	.570	30.275	.001	30.275	.996
	Current	.102	4	.026	1.357	.339	5.429	.243
	Ash %	.161	4	.040	2.136	.179	8.542	.367
	Duration	.001	1	.001	.043	.842	.043	.054
	Length	.046	1	.046	2.434	.163	2.434	.272
	Error	.132	7	.019				
	Total	5.428	18					
	C.Total	.465	17					

Mn	C.Model	.622(b)	8	.078	1.237	.425	9.899	.205
	Intercept	2.212	1	2.212	35.222	.002	35.222	.996
	Current	.015	2	.007	.116	.893	.232	.060
	Ash %	.147	4	.037	.585	.688	2.340	.111
	Duration	.095	1	.095	1.516	.273	1.516	.172
	Length	.084	1	.084	1.331	.301	1.331	.157
	Error	.314	5	.063				
	Total	11.342	14					
C.Total	.936	13						
Ni	C.Model	.209(b)	10	.021	1.678	.253	16.784	.356
	Intercept	1.063	1	1.063	85.508	.000	85.508	1.000
	Current	.111	4	.028	2.240	.166	8.961	.384
	Ash %	.073	4	.018	1.461	.310	5.843	.259
	Duration	.005	1	.005	.373	.561	.373	.083
	Length	.009	1	.009	.689	.434	.689	.111
	Error	.087	7	.012				
	Total	7.940	18					
C. Total	.296	17						
Pb	C.Model	1.401(b)	10	.140	4.350	.032	43.502	.784
	Intercept	2.119	1	2.119	65.785	.000	65.785	1.000
	Current	.787	4	.197	6.108	.019	24.434	.822
	Ash %	.568	4	.142	4.409	.043	17.635	.676
	Duration	.015	1	.015	.466	.517	.466	.091
	Length	.210	1	.210	6.513	.038	6.513	.593
	Error	.225	7	.032				
	Total	13.971	18					
C.Total	1.626	17						
Zn	C.Model	1.049(b)	10	.105	4.123	.028	41.230	.809
	Intercept	2.338	1	2.338	91.886	.000	91.886	1.000
	Current	.452	4	.113	4.446	.035	17.782	.717
	Ash %	.429	4	.107	4.219	.040	16.878	.692
	Duration	.021	1	.021	.837	.387	.837	.128
	Length	.293	1	.293	11.521	.009	11.521	.843
	Error	.204	8	.025				
	Total	14.650	19					
C.Total	1.253	18						

C.Total - Corrected Total; C. Model - Corrected Model

3.2. Electrolyte Development Over Time

3.2.1. First Regression

In an ideal EDR experiment, the content of heavy metals will increase in compartments I and III and decrease in compartment II, and hence the media can be considered remediated (Figure 1). In this chapter Cd, Cu, Pb and Zn migration to the compartments I and III of the electro-dialytic cell were observed throughout the remediation time. An attempt to predict the metals' behaviour was carried out. For this scenario, 9 experiments were selected and are shown in Table 8.

Cd, Cu, Pb and Zn behaviour were studied in compartment I (AN) and compartment III (CAT) separately. 4th degree polynomials were adjusted to each case, considering each metal that migrated either to compartment I (*Cd AN*, *Cu AN*, *Pb AN* and *Zn AN*) or compartment III (*Cd CAT*, *Cu CAT*, *Pb CAT* and *Zn CAT*).

Table 8. Resumé of experimental variables for the selected cases

Experiment	Ash %	Current (mA)	Duration (days)	Length (cm)
1	75	40	21	10
4	50	40	21	10
5	75	40	14	10
10	50	40	14	3
14	75	20	14	3
15	75	60	14	3
16	75	80	14	3
17	75	0	14	3
18	100	0	14	3

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

where $e_i \sim N(0, \sigma^2)$.

The parameters a_0 , a_1 and a_2 have a physical interpretation. The parameters a_3 and a_4 are not further considered. We point out that:

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 at which the metal enters the electrolyte compartments;

a_2 – measures the initial acceleration ($a_2 > 0$) or deceleration ($a_2 < 0$) of the migration, i.e. the rate at which one object/metal changes its migration velocity.

The a_1 values given by Table 9 were overall positive, meaning that metals enter the electrode compartments (both anode and cathode) throughout the experimental time and increase in concentration. A negative a_2 variable suggests

a decreasing velocity rate with time, while a positive a_2 means an increasing velocity rate. Table 9 shows no specific trend for a_2 . However, minor observations may be sketched. Cd velocity migration to the anode (compartment I) diminishes over time, having a higher velocity at the beginning of the EDR experiment.

3.2.2. Biregressional Method

To complete the analysis, a second regression series was adjusted. The controlled variables for these were the levels of "Ash %", "Current", "Duration", "Length", and the dependent variables the adjusted coefficients of the first set of regressions.

The objective of this methodology was to make inferences about the influence of the factors of the experiments on $a_0, a_1 \dots a_4$, i.e. mainly the initial concentration of the metal (a_0), the initial velocity at which the metal enters the electrolyte compartment (a_1) and the rate at which one object/metal changes its migration velocity (a_2).

Thus we adjusted 4th degree polynomials for each combination of metal and compartment in which it stands

$$y_i(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + e_i; i = 1, \dots, L$$

where $e_i \sim N(0, \sigma^2)$. With this set of regressions it was possible to take, for each treatment i , $i = 1, \dots, L$, a linear combination of the a_j , $j = 0, \dots, 4$, as observations. In particular, taking

$\mathbf{c}_i = [0 \dots 1 \dots 0]^t$, where 1 is in i -th position, thus obtaining

$$a_{i,j} = \mathbf{c}_{i+1} \mathbf{a}_j; j = 0, \dots, 4; i = 1, \dots, L.$$

Let λ_j , $j = 0, \dots, 4$, be the vectors of $a_{i,j}$, $i = 1, \dots, L$. Taking

$$\mathbf{T} = \begin{bmatrix} 1 & t_1 & \dots & t_1^4 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & t_n & \dots & t_n^4 \end{bmatrix},$$

Table 9. Parameters a_0, a_1, \dots, a_4 resulting from adjustment of 4th degree polynomial to each time series of each experiment on the electrolytes (catholyte and anolyte) for Cd, Cu, Pb and Zn

Polynomial Constants	Exp.	Cd AN	Cd CAT	Cu AN	Cu CAT	Pb AN	Pb CAT	Zn AN	Zn CAT
A0	1	0.0592	-0.1259	-0.1136	0.2189	0.5054	0.3215	1.0045	-3.1991
A0	4	-0.1515	-0.2125	-0.0994	-0.8867	-0.0196	-0.0715	-3.7765	-9.4265
A0	5	-0.4018	0.8627	0.0137	-0.0311	-0.5133	0.1031	-7.9752	20.3210
A0	10	-0.0252	-0.2197	-0.0294	-1.2973	0.2797	0.3109	-0.7740	-4.6046
A0	14	-0.0574	-0.1349	-0.0999	-0.3520	-0.0239	0.0674	-1.2013	3.7953
A0	15	-0.6552	-0.2187	-1.2985	-0.5895	-2.3823	-1.4595	-9.5205	-5.2063
A0	16	-0.3112	-0.5604	-1.1666	-0.4558	-0.4720	-1.2845	-8.0797	-18.2720
A0	17	-0.1515	-0.2125	-0.0994	-0.8867	-0.0196	-0.0715	-3.7765	-9.4265
A0	18	-0.0453	-0.2819	-0.0991	-0.2959	0.0126	-0.0954	-1.7472	-5.5780
A1	1	1.1987	0.7043	1.1355	0.3621	0.3811	1.1513	36.4220	22.8530
A1	4	0.2520	0.3367	0.1057	1.2596	0.0762	0.4070	5.8569	12.3780
A1	5	0.5639	-1.5905	-0.0733	0.1073	1.0176	0.1069	13.9450	-35.5970
A1	10	0.0763	0.5096	0.0786	1.8501	-0.4577	-0.3782	2.2741	12.1270
A1	14	0.1422	0.2963	0.2573	0.5988	0.0409	0.4289	3.1538	-7.5260
A1	15	0.9319	0.1675	1.7376	0.6671	3.2798	1.9184	11.2450	1.8895
A1	16	0.7141	0.8861	2.4336	0.6579	1.0506	1.9770	15.1700	28.8330
A1	17	0.2520	0.3367	0.1057	1.2596	0.0762	0.4070	5.8569	12.3780
A1	18	0.0934	0.3506	0.2539	0.2360	0.0156	0.8455	1.5436	7.5241
A2	1	-0.2043	-0.1237	-0.1799	-0.0669	-0.0774	-0.2345	-5.4060	-4.2328
A2	4	-0.0246	-0.0419	0.0448	-0.2488	0.0021	-0.0881	0.2680	-0.8875
A2	5	-0.0699	0.8062	0.0907	0.0698	-0.2746	0.0313	0.0828	18.5630

A2	10	-0.0094	-0.0289	0.0041	-0.2932	0.1567	0.1319	-0.4149	-0.2307
A2	14	-0.0173	-0.0225	0.0025	-0.1103	0.0049	-0.1066	-0.4822	4.1033
A2	15	-0.1667	0.0232	-0.1994	-0.0563	-0.5511	-0.4805	0.0094	3.6141
A2	16	-0.1368	-0.2988	-0.4353	-0.1533	-0.2179	-0.5478	-1.4570	-9.6416
A2	17	-0.0246	-0.0419	0.0448	-0.2488	0.0021	-0.0881	0.2680	-0.8875
A2	18	-0.0099	-0.0437	-0.0380	0.1155	0.0270	-0.1946	0.3593	-0.3113
A3	1	0.0123	0.0085	0.0099	0.0044	0.0052	0.0161	0.2803	0.3038
A3	4	0.0010	0.0023	-0.0038	0.0306	-0.0015	0.0097	-0.0764	-0.0281
A3	5	0.0008	-0.1015	-0.0126	-0.0140	0.0257	-0.0072	-0.2309	-2.3159
A3	10	0.0007	-0.0003	-0.0010	0.0132	-0.0119	-0.0112	0.0360	-0.0444
A3	14	0.0010	0.0012	-0.0019	0.0070	-0.0005	0.0094	0.0339	-0.4355
A3	15	0.0108	-0.0048	0.0048	-0.0011	0.0328	0.0476	-0.1644	-0.5774
A3	16	0.0108	0.0349	0.0352	0.0140	0.0160	0.0544	0.0052	1.1674
A3	17	0.0010	0.0023	-0.0038	0.0306	-0.0015	0.0097	-0.0764	-0.0281
A3	18	0.0008	0.0028	0.0044	-0.0146	-0.0033	0.0232	-0.0585	-0.0282
A4	1	-0.0002	-0.0002	-0.0002	-0.0001	-0.0001	-0.0004	-0.0047	-0.0070
A4	4	-0.00002	-0.00005	0.00008	-0.0013	0.0001	-0.0004	0.0028	0.0030
A4	5	0.0001	0.0037	0.0005	0.0006	-0.0008	0.0003	0.0118	0.0828
A4	10	-0.00002	0.00004	0.00003	-0.00008	0.0003	0.0003	-0.0011	0.0016
A4	14	-0.00003	-0.00004	0.00007	-0.0001	0.00002	-0.0003	-0.0009	0.0137
A4	15	-0.0002	0.0002	0.00009	0.0001	-0.0007	-0.0015	0.0080	0.0238
A4	16	-0.00030	-0.0013	-0.0011	-0.0004	-0.0003	-0.0018	0.0021	-0.0430
A4	17	-0.00002	-0.00005	0.00008	-0.0013	0.0001	-0.0004	0.0028	0.0030
A4	18	-0.00003	-0.00007	-0.0002	0.0005	0.0001	-0.0009	0.0022	0.0017

Bold - values not considered for R^2 coefficient of determination inferior to 0.70; P.C. - Polynomial Constants

it was easy to conclude, assuming that each $a_{i,j}$ was a function of the factors in the experiment, that $\lambda_j \sim N(\mathbf{X}\beta_j, k_j\sigma^2\mathbf{I})$, $j=0, \dots, 4$,

$$k_j = \mathbf{c}_j(\mathbf{T}'\mathbf{T})^{-1}\mathbf{c}_j.$$

It was then trivial to adjust a usual linear regression, where the model matrix \mathbf{X} for this regression had the column vectors associated with the factors.

Each α and its corresponding t values are given in Table 10. In an overall interpretation, the influence of the studied variables “Ash %”, “Current”, “Duration” and “Length” may be significantly ($\alpha < 0.05$) positive or negative in respect of the performance of each parameter a_0 , a_1 and a_2 .

In the migration to compartment I, it can be seen that none of the studied variables had a significant impact on *Pb AN* (Table 10). For *Cd AN* experiment “Duration” had an influence on a_2 . In *Cu AN* and *Zn AN* migration, “Current” influenced significantly a_0 , a_1 and a_2 . As for migration to compartment III, none of the studied variables had significant influence ($\alpha < 0.05$) on *Cd CAT* and *Zn CAT*. Regarding *Cu CAT*, the variable “Ash %” influenced significantly a_0 , a_1 and a_2 , while *Pb CAT* was significantly influenced by “Current” in all of a_0 , a_1 , and a_2 .

If we consider *Cu AN* or *Zn AN* migration, the interpretation of Table 10 may be as follows: the higher the applied “Current”, the less changeable the initial concentration (a_0) on the anolyte ($t < 0$), meaning no need for a correction factor; the higher the migration velocity (a_1) of metals Cu and Zn to the anode ($t > 0$); and the lower the rate of variation of velocity (a_2) ($t < 0$). If a_2 has $t < 0$ this means that with increasing “Current” the migration velocity of *Cu AN* or *Zn AN* continuously decreases along the time series. This interpretation is valid for any variable with $\alpha < 0.05$, with the t value positive or negative.

Analysing the second group of regressions (Table 10), it can be seen that the different variables have different effects on each metal, and whether it migrates towards the anode or the cathode. In the EDR process, the migration of metals is influenced by different chemical conditions, including its complexation. If the metal is bound predominantly in a negative complex, the metal will show up in higher concentrations in the compartment I solution (anolyte). However, if metals are mainly positive and migrate to compartment III (cathode), they will probably deposit on the electrode, experiencing an immediate decrease in solution concentration (catholyte). Therefore, the different studied variables may have different effects on each metal, depending on its complexation. According to Lima et al. (2005), the complexes formed by MSWI fly ash and 0.25M ammonium citrate in 1.25% NH_3 are for Cd: $\text{Cd}(\text{Cit})\text{OH}^{2-}$ and $\text{Cd}(\text{NH}_3)_4^{2+}$; for Cu: $\text{Cu}(\text{NH}_3)_3\text{OH}^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$; and for Zn: $\text{Zn}(\text{CO}_3)_2^{2-}$ and $\text{Zn}(\text{NH}_3)_4^{2+}$. Pb was not included in this study.

As regards *Cd AN* (Table 10), the variable “Duration” significantly decelerated its migration to compartment I. As for *Cu*, “Current” influenced *Cu AN* migration to compartment I and “Ash %” and “Length” *Cu CAT* to compartment III. “Current” influenced *Pb CAT* migration as well as *Zn AN* migration, but for different compartments. Finally, “Duration” influenced *Zn AN* (Table 10).

In Lima et al. (2005) *Cd* shows up as ionic compounds $\text{Cd}(\text{Cit})\text{OH}^{2-}$ and $\text{Cd}(\text{NH}_3)_4^{2-}$, complexing with the citrate and ammonia of the assisting agent (0.25M ammonium citrate in 1.25% NH_3). The expected migration is to compartment I, hence to the anode. According to Table 10, “Duration” significantly ($\alpha < 0.05$) and negatively ($t < 0$) affects *Cd* acceleration (a_2) to the anode, i.e. the higher the “Duration” of an EDR experiment, the lower the rate of variation of *Cd* migration velocity. This means that with increasing remediation time the slope of migration velocity will decrease and therefore its variation will be negative, i.e. migration velocity tends to decrease to a null value. In terms of EDR removal the biregressional model tells us that *Cd* will migrate to the anode for a limited extent of the remediation time, probably coinciding with the available ionic forms $\text{Cd}(\text{Cit})\text{OH}^{2-}$ and $\text{Cd}(\text{NH}_3)_4^{2-}$ present in solution in the central compartment.

Cu is expected to complex as $\text{Cu}(\text{NH}_3)_3\text{OH}^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$, combining with the ammonia of the assisting agent. The expected migration is to compartment III, the cathode. Table 10 shows significant ($\alpha < 0.05$) *Cu* migration to both compartments I and III. This reveals negative and mobile forms of *Cu* present in solution, migrating to compartment I. “Current” was a variable affecting *Cu AN*, meaning that with increasing “Current”, the velocity of *Cu* migration to the anode increases until a certain level is reached. As for *Cu CAT*, the variables “(central compartment) Length” and “Ash %” affect significantly ($\alpha < 0.05$) and negatively ($t < 0$) *Cu* migration velocity (a_1). This means that, with increasing “Ash %” and “Length”, *Cu* migration velocity decreases. However “Ash %” presents a positive influence on acceleration (a_2). This means that with increasing “Ash %”, *Cu* migration decreases, and its variation will continuously increase. Overall, increasing central compartment “Length” and the “Ash %” will negatively affect *Cu* remediation.

Table 10. Linear regression to each $a0, a1, \dots, a4$ of the previous regressions (table 10) to Cd, Cu, Pb and Zn, in anode and cathode compartments, in relation to each variable

	Cd AN		Cd CAT		Cu AN		Cu CAT		Pb AN		Pb CAT		Zn AN		Zn CAT	
	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value	t	p-value
a0	Current	-1.97	0.120	-0.29	0.787	-3.92	0.017	1.46	0.218	-1.52	0.203	-3.20	0.033	-2.82	0.048	0.697
	Ash %	-1.11	0.329	0.64	0.559	-1.39	0.238	4.48	0.011	-0.87	0.432	-1.54	0.200	-1.70	0.164	0.624
	Duration	1.61	0.183	-1.10	0.335	0.18	0.863	1.31	0.260	0.92	0.408	0.95	0.396	2.61	0.059	0.524
	Length	-0.60	0.581	2.06	0.109	1.49	0.209	2.56	0.063	0.05	0.962	0.89	0.423	-1.11	0.328	0.242
a1	Current	3.08	0.037	0.10	0.926	5.57	0.005	-2.09	0.104	1.89	0.132	2.87	0.046	3.32	0.029	0.750
	Ash %	1.52	0.204	-1.00	0.375	2.06	0.108	-6.54	0.003	1.15	0.312	2.12	0.101	1.72	0.161	0.494
	Duration	2.33	0.080	1.89	0.132	1.75	0.155	0.60	0.579	-0.42	0.694	0.69	0.530	5.57	0.005	0.187
	Length	0.44	0.682	-2.26	0.087	-2.19	0.094	-3.28	0.030	0.11	0.917	-0.74	0.502	1.40	0.234	0.197
a2	Current	-3.91	0.017	-0.19	0.861	-5.00	0.007	0.81	0.461	-2.20	0.092	-2.79	0.049	-2.28	0.085	0.718
	Ash %	-1.73	0.159	0.75	0.495	-1.88	0.133	4.56	0.010	-1.59	0.188	-1.94	0.124	0.06	0.953	0.599
	Duration	-2.90	0.044	-1.53	0.200	-2.05	0.109	-0.98	0.380	0.66	0.545	-0.49	0.652	-9.29	0.001	0.229
	Length	0.19	0.859	2.03	0.112	2.39	0.075	2.17	0.096	-0.60	0.580	0.87	0.432	1.39	0.237	0.189
a3	Current	4.73	0.009	0.21	0.843	2.53	0.064	-0.65	0.554	2.49	0.068	2.50	0.067	-0.45	0.679	0.693
	Ash %	1.64	0.177	-0.71	0.515	0.94	0.402	-2.06	0.109	1.95	0.123	1.77	0.152	-1.35	0.248	0.620
	Duration	3.58	0.023	1.43	0.225	1.14	0.319	0.36	0.739	-0.97	0.388	0.22	0.840	4.37	0.012	0.254
	Length	-1.57	0.191	-2.02	0.113	-1.53	0.201	-0.71	0.516	1.12	0.326	-1.00	0.375	-2.03	0.113	0.178
a4	Current	-3.42	0.027	-0.24	0.820	-1.57	0.191	0.67	0.539	-2.22	0.090	-2.17	0.096	1.08	0.340	0.682
	Ash %	-0.77	0.486	0.70	0.524	-0.57	0.598	1.39	0.236	-1.99	0.117	-1.60	0.185	1.63	0.179	0.628
	Duration	-2.46	0.069	-1.38	0.241	-0.75	0.495	-0.12	0.912	1.15	0.313	-0.04	0.971	-2.99	0.040	0.277
	Length	2.34	0.079	2.03	0.113	1.19	0.301	0.26	0.806	-1.50	0.208	1.00	0.372	2.09	0.105	0.176

Bold – Significant values with $\alpha < 0.05$

For Pb, a similar situation is observed as for Cu, where increasing applied "Current" diminishes EDR remediation of Pb from fly ashes. The selected assisting agent (0.25M ammonium citrate in 1.25% NH₃) did not affect Zn migration, since the variables only affected Zn AN, i.e. the negative species present in the matrix migration (Zn(CO₃)₂²⁻). "Current" and "Duration" were the variables influencing Zn AN migration, positively (t>0) affecting its migration velocity (*aI*) to compartment I.

4. Overall Discussion

From the F tests and Scheffé's multiple comparison method the following was observed:

- "Duration" is the one variable that had no significant influence on EDR efficiency, meaning that shorter experimental periods do not represent inferior removal efficiencies when compared with longer periods (14 vs. 21 days).
- Defining "Metal" as a variable, we might conclude that the process efficiency depends on the metal.
- Out of all variables, "Current" and "Length" had the highest influence on EDR remediation of fly ash, followed by "Ash %".
- "Current" and "Ash %" significantly influence Cu, Pb and Zn migration and the most efficient values would be 80mA and 75%, respectively. Cr is more influenced by "Current" where Cd is more influenced by "Length".
- "Length", the shorter the distance between electrodes, the higher the removal efficiencies.

From the biregressional study the overall conclusion would be that:

- there is no need to extend experiment "Duration" in order for Cd to continuously increase in the anolyte;
- with increasing "Current" Cu migration velocity increases to the anode, and a low central compartment "Length" and a low "Ash %" increases Cu migration to the cathode;
- the higher the applied "Current", the higher Pb migration velocity to the cathode;
- and with increasing applied "Current" and experiment "Duration", Zn migration velocity increases to the anode.

When considering electrodiolytic remediation, the equated variables have to be a function of the ionic metal species present on the matrix to be remediated. That is to say, a certain variable will affect the ionized metal specie (positive or negative), and not the metal as a whole. It is then advantageous for study to use a chemical program to predict the metal species formed between the contaminated matrix and the assisting agent before conducting the experiments and hence adjust

the variables to the metal's removal. This study helped to eliminate the variables "Duration" from the remediation of fly ashes and focus on "Current" and "Ash %".

REFERENCES

- Ferreira C., Ribeiro A., Ottosen L. (2003). Possible applications for municipal solid waste fly ash. *J. Hazard. Mater.* B96, 201-216.
- Hansen H.K., Ottosen L.M., Kliem B.K., Villumsen A. (1997). Electrokinetic Remediation of Soils Polluted with Cu, Cr, Hg, Pb and Zn. *J. Chem. Tech. Biotech* 70, 67-73.
- Lima A.T., Varela-Castro A., Ribeiro A.B., Castelo Branco M.A., Domingues H., Monteiro O.R., Ottosen L.M. (2005). An attempt to predict the behavior of Cu, Zn and Cd during electro dialytic process. ChemPor-9th International Chemical Engineering Congress, Coimbra, Portugal, 21-23 September 2005, QL019, pp. 365 in Book of Abstracts and 6 pp. in CD-ROM
- Mexia J.T. (1990). Best linear unbiased estimators, duality of F tests and the Scheffé multiple comparison method in presence of controlled heterocedasticity, *Comp. Stat and Data Analysis*, Vol. 10, nº 3.
- Moreira E.E., Ribeiro A.B., Mateus E.P., Mexia J.T., Ottosen L.M. (2005a). Regressional modeling of electro dialytic removal of Cu, Cr and As from CCA treated timber waste: application to sawdust, *Wood Sci. Tech.* 39, 291- 309.
- Moreira E.E., Ribeiro A.B., Mateus E.P., Mexia J.T., Ottosen L.M. (2005b). Regressional modelling of electro dialytic removal of Cu, Cr and As from CCA timber waste: application to wood chips, *Biometrical letters* , Vol. 42, nº1, pp 11-25.
- Nystroem G.M., Ottosen L.M., Villumsen A. (2005). Electro dialytic removal of Cu, Zn, Pb and Cd from harbour sediment—the influence of changing experimental conditions. *Environ. Sci. Tech.* 39, 2906–11.
- Ottosen L.M., Hansen H.K., Laursen S., Villumsen A. (1997). Electro dialytic Remediation of Soil Polluted with Copper from Wood Preservation Industry, *Environ. Sci. Tech.* 31, 1711-1715
- Ottosen L.M., Hansen H.K. (1992). Electrokinetic cleaning of heavy metals polluted soil. Internal Report, Fysisk-Kemisk Institut for Geologi og Geoteknik, Technical University of Denmark, Denmark, 9pp.
- Ribeiro A.B., Mexia J.T. (1997). A dynamic model for the electrokinetic removal of copper from a polluted soil. *J. Hazard. Mater.* 56, 257-271
- Ribeiro A.B. (1998). Use of Electro dialytic remediation technique for removal of selected heavy metals and metalloids from soils, Department of Civil Engineering – Technical University of Denmark; PhD Thesis.
- Ribeiro A.B., Mateus, E.P., Ottosen, L.M., Bech-Nielsen, G. (2000). Electro dialytic removal of Cu, Cr and As from chromated copper arsenate-treated timber waste. *Environ. Sci. Tech.* 34(5), 784-788.
- Pedersen A.J. (2003). Characterization and electro dialytic treatment of wood combustion fly ash for the removal of cadmium. *Biomass Bioenerg.* 25, 447–58.
- SPSS INC. (1989). SPSS, version 1 September 2004. Apache Software Foundation, LEADTOOLSou, Chicago, Illinois.