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ORIGINAL PAPER

Experimental and modeling of the electrodialytic and dialytic treatment of a fly ash containing Cd, Cu and Pb

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Abstract A one-dimensional model is developed for simulating the electrodialytic and dialytic treatment of a fly ash containing cadmium, copper and lead. Two experimental systems have been used, a column of ash and a stirred ash suspension. The movement of Cd, Cu and Pb has been modeled taking into account the diffusion transport resulting from the concentration gradients of their compounds through the membranes and boundary layers and the electromigration of their ionic, simple and complex species during the operation. The model also includes the electromigration of the non-contaminant most important principal ionic species in the system, H^+ and OH^-, proceeding of the electrolysis at the electrodes, Ca^{2+}, $CO_3^{=}$, $SO_4^{=}$, etc. proceeding from the ash and Na^+ and NO_3^-, or citrate and ammonium ions incorporated as electrolyte solutions and/or as agent solution during the ash treatment. The simulation also takes into account that OH^- generated on the cathode, during the electrodialytic remediation, is periodically neutralized by the addition of nitric acid in the cathode compartment. The anion and cation-exchange membranes are simply represented as ionic filters that preclude the transport of the cations and anions, respectively, with the exception of H^+ which is retarded but pass through the anion-exchange membrane.

Keywords Electroremediation · MSW-fly ash · Heavy metals · Modeling

1 Introduction

Incineration is a growing treatment solution for some residues, especially for municipal solid waste (MSW). This technology outputs fly ash, which is considered an hazardous waste [1], due to its heavy metal content, among other pollutants. Current practice in many countries implies inertization of fly ash followed by landfill disposal, which represents a waste of raw material, energy, area, without knowing the actual long term environmental risks. According to Wiles [2] and Ferreira et al. [3] incineration gather a series of characteristics that could be valued in construction materials, geotechnical applications or soil conditioning, but ashes should not exhibit any hazardous characteristic.

The electrodialytic (ED) process is a remediation technique for removal of contaminants from porous media and it has been applied to several matrices since it was first described for heavy metal contaminated soil [4]. ED is a combination of electrokinetics and dialysis, where principles such as electroosmosis, electromigration (EM) and electrophoresis take action [5, 6]. Fly ash has been submitted to ED by several authors, who tried different

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approaches for their remediation [7–9] using, for instances, various assisting agents, from which 0.25 M ammonium citrate in 1.25% ammonia has shown to be the most effective.

In a dialytic (DI) process, ion-exchange membranes are used in order to regulate the ion transfer from a polluted matrix suspension into a contiguous compartment, where a lower salt concentrated solution is placed [10, 11]. The driving force in dialysis is a concentration gradient, where concentration differences between two subsequent solutions dictate the migration of ions, flowing from a high to a low concentration medium [12].

The present work compares the removal of cadmium (Cd), copper (Cu) and lead (Pb) out of a stationary fly ash column versus a suspended fly ash, induced by a chemical gradient alone (dialytic) and by both chemical and external potential gradients in combination (electrodialytic). Moreover, a comparison between the use of water and 0.25 M ammonium citrate in 1.25% ammonia is carried out.

In our previous studies, a comparison between ED and DI processes was carried out for the remediation of CCA treated wood [11, 13]. The present work extends those ones, adding the following new features: (i) the use of different assisting agents; (ii) the comparison between a stationary cell and a stirring cell, which is closer to pure electrodialysis/dialysis; (iii) the development of a one-dimensional model for simulating the ED and DI treatment of a fly ash containing Cd, Cu and Pb, incorporating information obtained by chemical characterization, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), as well as by previous equilibrium simulation using Visual Minteq at zero time.

2 Materials and methods

2.1 Polluted material

Laboratory experiments were carried out with fly ash, sampled in VALORSUL, the Portuguese MSW incinerator that serves the Lisbon region. This fly ash results from the complete flue gas treatment at the incineration unit: injection of ammonia for NO_x removal in the boiler; addition of lime in the scrubber; collection of all the formed particulates (both electrically and non-electrically chargeable) in filters [14]. The "total" studied metal contents in the ash were 82 ± 12 mg of Cd kg^{-1}, 543 ± 50 mg of Cu kg^{-1} and 2644 ± 218 mg of Pb kg^{-1} on dry basis.

2.2 Laboratory cell

Laboratory experiments were carried out in an ED cell schematically shown in Fig. 1, based on a concept developed at the Technical University of Denmark [4] and described in detail elsewhere [5, 11]. The ED cell is divided into three compartments, consisting of two electrode compartments (I and III) and a central one (II) of L = 10 cm (stirred batch) or 3.8 cm (column), internal diameter = 8 cm. Compartments I and II were separated by an anion-exchange membrane (204 SZRA B02249C, from Ionics) and II and III by a cation-exchange membrane (CR67HUYN12116B, from Ionics). Peristaltic pumps circulated the electrolytes in compartments I and III. The working electrodes were platinised titanium bars from Permaskand, with a diameter of 3 mm and length of 5 cm. A power supply (Hewlett-Packard E3612A) was used to adjust the desired initial direct current and was monitored by a Fluke 37 multimeter.

2.3 Experimental conditions

Six experiments of 14 days duration, using 100 g (90 g in experiments 1–2) of fly ash with the assisting agents, three under ED and three under DI (no external power supply) conditions, were performed as summarised in Table 1. A stationary cell (Fig. 1a) was used for experiments one and two, whereas a stirring cell system (Fig. 1b) for experiments 3–6. The fly ash was placed in compartment II of the cell.

When the stirred batch experiments (experiments 3–6), the fly ash was introduced in the cell after its static incubation in the assisting agent for 24 h experiments, in a L/S phase ratio (w/w), according to Table 1. After incubation and fly ash deposition, the leachate was separated through

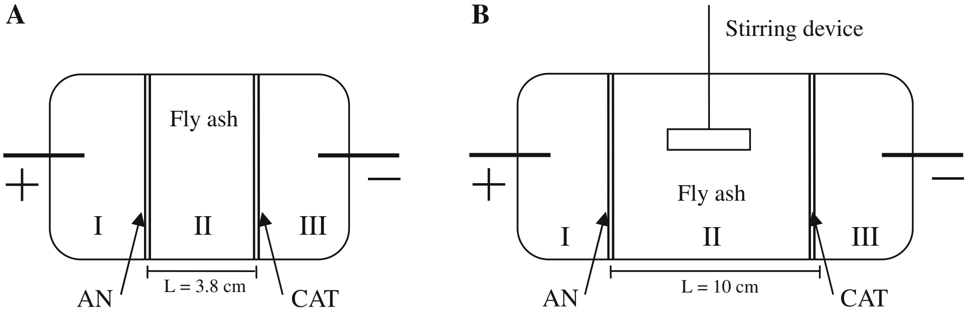

Fig. 1 Schematic representation of the electrodialytic cell. **a** Unstirred ash and **b** stirred ash suspension. *AN* anion-exchange membrane, *CAT* cation-exchange membrane, *I* anode compartment, *II* central compartment, *III* cathode compartment

Table 1 Experimental conditions

Test	Setup design	Assisting agent	Intensity (mA)	Anolyte	L/S
1	A	0.25 M amm. cit.	40	0.25 M amm. cit.	1:16
2	A	0.25 M amm. cit.	0	0.25 M amm. cit.	1:16
3	B	Distilled water	40	0.01 M $NaNO_3$ at pH = 2	4
4	B	Distilled water	0	0.01 M $NaNO_3$ at pH = 2	4
5	B	0.25 M amm. cit.	40	0.25 M amm. cit.	4
6	B	0.25 M amm. cit.	0	0.25 M amm. cit.	4

Catholyte was constant in all experimental tests (0.01 M $NaNO_3$ at pH = 2) and anolyte differs, 0.25 M amm. cit. in 1.25% ammonia

decantation, and Cd, Cu and Pb concentrations measured in the leachate.

In the stirring cell system, the suspensions were stirred by a "Heto" motor with a rotation velocity of 1300 rpm, since compartment II had a hole in the centre, where a flexible plastic flap (approx. L = 5 cm and 6 mm width) was fastened to an insulated wire.

Through each electrode compartment, 1 L of 10^{-2} M $NaNO_3$ was always used as catholyte, whereas 1 L of anolyte varied according to Table 1. The pH value of the catholyte solution was adjusted to about two by periodical addition of concentrated HNO_3 solution, both in the DI as in the ED experiments. Anolyte pH was not adjusted during experimental time. Samples from the electrolytes were collected periodically, stored in refrigerated PVC vials for Cd, Cu, Pb and pH measurements.

At the end of each experiment, fly ash from compartment II was filtrated by 0.45 μm filter and collected for analysis, as well as the electrodes and membranes that were rinsed in 5 M HNO_3 and 1 M HNO_3, respectively. Volume of the electrolytes and metal content in the electrolytes from the three compartments were also measured.

2.4 Analytical methods

Cadmium, Cu and Pb in solution were determined by Atomic Absorption Spectrophotometry (Perkin Elmer 5000-AAS). The "total" amount of each element in fly ash, before and after the experiments, was similarly analysed by AAS, after a microwave assisted pressurized digestion in concentrated HNO_3 (0.25 g fly ash + 10 mL HNO_3), followed by a vacuum filtration through 0.45 μm filter, diluted to 50 mL. In the analytical scheme, the NIST 2690 Coal fly ash reference material was incorporated. Fly ash chloride content and pH were measured in water in a liquid/solid (L/S) ratio of 1/2.5, using a Dionex ion chromatograf (DX120) and a pH electrode, respectively. Gas production, or carbonate content, from 2.5 g of fly ash in 20 mL of 10% HCl was measured using a Bascomb calcimeter. Three replicates of each parameter were carried out. Further characterization of the initial fly ash using, for instance, the [15] standard, can be found elsewhere [16].

3 Process simulation and model description

3.1 Preliminary calculations

Table 2 presents the estimated fly ash composition using the information obtained by previous chemical characterization and analysis by XRD and by XPS. Afterwards, the ash pre-washing process has been simulated by mean of the Visual Minteq code that allows the calculation of the soluble species to be removed with the aqueous phase and the remaining or precipitated solid species to be decontaminated by ED or DI processes. Thus, these last species constitute the initial ones to be treated in the ED and DI stirred experiments (Table 3). The comparison between the experimental and modeling results of the pre-washing operation are presented in Table 4.

It can be seen that the weight losses (%) given by experimental and calculated values are very similar if distillated water is used as a pre-washing-agent. In addition, the chloride and Cd concentrations, experimental and calculated, in both pre-washing solutions are rather similar (Table 4), and mainly if we take into account the high heterogeneity of the material. On the opposite, the concentrations of the other heavy metals, particularly Pb, show a very different behaviour in reality when compared with predictions by expected equilibria.

These differences between experimental and calculated values can be attributed to the presence of the some ions (Pb, Cu, Cd, Ca, Cl, etc.) partially forming any species non-identified by XRD or XPS (Table 2).

3.2 Model description

The model operates in two steps, first simulating the kinetic process by integrating forward in time one-dimensional transport equations, including electrochemical reactions (ERs) and, after that, reestablishing the chemical equilibria before the next step of integration. This is done because

Table 2 Estimated fly ash composition using the information obtained by previous chemical characterization and analysis by XRD and by XPS

Principal species	Content (%)	Compound	Identified by	Estimated content (g/100 g)
SiO_2	29	Quartz, SiO_2	XRD	29
Ca^{2+}	22.7	Lime, CaO	XPS	15.4
Na^{+}	3.4	Halite, NaCl	XRD and XPS	8.7
K^{+}	3.4	Sylvinite, KCl	XRD and XPS	6.5
Cl^{-}	13.1	Calcium chloride, $CaCl_2$	XPS	7.4
$SO_4^{=}$	8	Anhydrite, $CaSO_4$	XRD	11.3
$CO_3^{=}$	7.25	Calcite, $CaCO_3$	XRD	12.1
PO_4^{3-}	2.1	Calcium hydrogen phosphate, $CaHPO_4$	XPS	3.0
Al^{3+}	2.4	Corundum, Al_2O_3	XRD and XPS	4.5
Zn^{2+}	0.6	Zinc chloride, $ZnCl_2$	XPS	1.3
Heavy metals	Content (mg kg^{-1})	Compound	Identified by	Estimated content (g/100 g)
Pb^{2+}	2644	Lead chloride, $PbCl_2$	XPS	0.355
Cu^{2+}	543	Copper chloride, $CuCl_2$	XPS	0.115
Cd^{2+}	82	Cadmium chloride, $CdCl_2$	XPS	0.012

Table 3 Calculated solid compounds simulated by Visual Minteq code to be treated in the ED and DI stirred experiments

Pre-washing agent	Calculated solid compound	Content (% initial ash)
Distilled water	Calcite, $CaCO_3$	12.1
	Gypsum, $CaSO_4{\cdot}2H_2O$	11.3
	Hydroxiapatite, $Ca_5OH(PO_4)_3$	1.2
	Portlandite, $Ca(OH)_2$	18.5
	Diaspore, AlOOH	5.3
	Quartz, SiO_2	29
	Total	77.4
Ammonium citrate	Calcite, $CaCO_3$	12.1
	Gypsum, $CaSO_4{\cdot}2H_2O$	12.2
	Hydroxiapatite, $Ca_5OH(PO_4)_3$	1.2
	Portlandite, $Ca(OH)_2$	8.8
	Diaspore, AlOOH	5.3
	Quartz, SiO_2	29
	Total	68.7

chemical equilibria are considered instantaneous if compared with the transport phenomena. Tables 5 and 6 show the most important ionic species and equilibriums used in the simulation. These ones were obtained using Visual Minteq, through previous simulation in a static way.

The mass conservation equation for ith species in a jth volume element, including ERs, is described by:

$$V_j\left(\frac{dc_{ij}}{dt}\right) = \left(N_{i,j-1}+N_{i,j+1}\right)A + R_iV_j \tag{1}$$

where V_j volume of water in jth cell (cm^3), c_{ij} is the concentration of ith species in the jth volume element (mol cm^{-3}), t is the time, $N_{i,\,j-1}$ and $N_{i,\,j+1}$ the mass flux of ith species from (j − 1)th and (j + 1)th element volume into jth volume element (mol cm^2 s^{-1}), A cross-sectional area of column (cm^2), and R_i the reaction rate for i species.

Only two transport phenomena are considered between each two compartments: ED and diffusive transport. The stirred compartment is assumed to be perfectly mixed. In the electrode compartments the assumption on a perfect mixture and ion generation by ERs is also considered.

Advective transport is present in the electrode compartments, through the recirculation of the electrolyte and the addition of acid for the pH control of the system.

3.2.1 Electrochemical reactions

We assume that the only ERs which need to be taken into account in the system are the reduction and oxidation of water on the electrodes and that the activity coefficients of all species can be assumed equal to unity.

The half-reaction at the cathode is

$$H_2O + 2e^- \rightarrow 2OH^-(aq) + H_2(gas) \quad E^0 = -0.828\,V \tag{2}$$

And the anode half-reaction is:

$$H_2O \rightarrow 4H^+(aq) + O_2(gas) + 4e^- \quad E^0 = -1.229\,V \tag{3}$$

Then, the ERs must be included in the mass balance equations of anode and cathode compartments

$$V_0\left(\frac{dc_{10}}{dt}\right)_{ER} = V_{N+1}\left(\frac{dc_{2N+1}}{dt}\right)_{ER} = \frac{I}{F}\eta \tag{4}$$

where V_0 and V_{N+1} are the volumes of electrolyte in the electrode compartments (≈1000 cm^3), c_{10} and c_{2N+1}, H^+ and OH^- concentrations generated there by ER, I is the current intensity, F, the Faraday's constant and η the

Table 4 Comparison between the experimental and modeling results of the pre-washing operation

Pre-washing agent		Experimental	Calculated	Percentage of error
Distilled water		Weight loss (%):		Absolute value:
		23.0	22.6	1.7
		Content in aqueous phase (mg L^{-1})		
	Cd	0.04	0.03	25.0
	Cu	0.43	0.01	97.7
	Pb	135.8	0.004	100.0
	Cl	27195	20873	23.2
Ammonium citrate		Weight loss (%):		Absolute value:
		10.45	31.3	199.5
		Content in aqueous phase (mg L^{-1})		
	Cd	12.3	22.7	84.6
	Cu	42.6	133.1	212.4
	Pb	51.3	0.004	100.0
	Cl	17317	20873	20.5

Table 5 Chemical equilibria in the system (concentrations: mol L^{-1})

Reaction	Log *K* formation	Source
Water ionization		
$H^+ + OH^- \rightleftarrows H_2O$	13.99	[23]
Acid dissociation		
$H_2CO_3 \rightleftarrows H^+ + HCO_3{}^-$		
$HCO_3^- \rightleftarrows H^+ + CO_3{}^{2-}$		
$H^+ + Cit^{3-} \rightleftarrows H(Cit)^{2-}$	6.396	NIST 46.6
$2H^+ + Cit^{3-} \rightleftarrows H_2(Cit)^-$	11.157	NIST 46.6
$3H^+ + Cit^{3-} \rightleftarrows H_3(Cit)(aq)$	14.285	NIST 46.6
Precipitation-dissolution		
$Cd^{2+} - 2H^+ + 2H_2O^- \rightleftarrows Cd(OH)_2$	13.644	NIST 46.7
$Cd^{2+} + CO_3{}^{2-} \rightleftarrows CdCO_3$	−12.01	PreGa01
$Pb^{2+} - 2H^+ + 2H_2O \rightleftarrows Pb(OH)_2$	8.15	MTQ3.11
$Cu^{2+} - 2H^+ + 2H_2O^- \rightleftarrows Cu(OH)_2$[Tenorite (c)]	7.64	PlyWZM97
$Ca^{2+} - 2H^+ + 2H_2O^- \rightleftarrows Ca(OH)_2$ [Portlandite]	22.704	NIST 46.7
$Ca^{2+} + CO_3{}^{2-} \rightleftarrows CaCO_3$ [Calcite]	−8.48	PlumBus82
$Ca^{2+} + SO_4{}^{2-} + 2H_2O \rightleftarrows CaSO_4 \cdot 2H_2O$ [Gypsum]	−4.61	NIST 46.7
$5Ca^{2+} + 3PO_4^{3-} - H^+ + H_2O \rightleftarrows Ca_5OH(PO_4)_3$ [Hydroxyapatite]	−44.333	NIST 46.7
$H_4SiO_4 - H^+ \rightleftarrows H_3SiO_4{}^-$	−9.84	NIST 46.4

Faradic efficiency that here describes the yield with which electrons (charge) transferred in the system are used by the ERs to produce H^+ or OH^-.

3.2.2 Electromigration transport of ions

Next, the EM of ions into a general *j*th volume element through its left side is analyzed. To do this, it is assumed that the cations are incoming in the cell from the $(j-1)$th cell, and simultaneously anions are moving out to that volume element crossing this one. Now, assuming perfect mixing in the cell and using the transport number, a typical electrochemical parameter, which represents the fraction of the current intensity (or the charge) carried by a particular ion [11, 17, 18]:

$$t_{i,j-1} = \frac{\lambda_i \left[c_{i,j-1} S(z_i) S\left(c_{i,j-1}\right) + c_{ij} S(-z_i) S\left(c_{i,j}\right)\right]}{\sum_{i=1}^{n} \lambda_i \left[c_{ij-1} S(z_i) S\left(c_{i,j-1}\right) + c_{ij} S(-z_i) S\left(c_{i,j}\right)\right]} \quad (5)$$

Table 6 Chemical equilibria in the system (concentrations: mol L^{-1})

Reaction	Log *K* Formation	Source
Complex formation		
$Al^{3+} - 4H^+ + 2H_2O^- \rightleftarrows Al(OH)_4^-$	−23	Wes92
$Ca^{2+} + Cl^- \rightleftarrows CaCl^+$	0.40	NIST 46.7
$Ca^{2+} + PO_4^{3-} \rightleftarrows CaPO_4{}^-$	6.46	SCD3.02(1993GMa)
$Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_4\,(aq)$	2.36	NIST 46.7
$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3(aq)$	3.22	PlumBus82
$Cd^{2+} - 2H^+ + 2H_2O^- \rightleftarrows Cd(OH)_2(aq)$	−20.294	NIST 46.7
$Cd^{2+} - 3H^+ + 3H_2O^- \rightleftarrows Cd(OH)_3{}^-$	−33.3	ParkApp99
$Cu^{2+} - 4H^+ + 4H_2O^- \rightleftarrows Cu\left(OH)_4{}^{2-}\right.\,(aq)$	−39.73	PlyWZM97
$Cu^{2+} - 3H^+ + 3H_2O^- \rightleftarrows Cu(OH)_3{}^-(aq)$	−26.64	PlyWZM97
$Pb^{2+} - 3H^+ + 3H_2O \rightleftarrows Pb(OH)_3^-$	−28.091	NIST 46.7
$Ca^{2+} + Cit^{3-} \rightleftarrows Ca(Cit)^-$	4.87	NIST 46.6
$Ca^{2+} + 2H^+ + Cit^{3-} \rightleftarrows CaH_2(Cit)^+$	12.59	NIST 46.6
$Ca^{2+} + H^+ + Cit^{3-} \rightleftarrows CaH(Cit)$	9.256	NIST 46.6

where λ_i is molar conductivity of *i*th ion (ohm^{-1} mol^{-1} cm^2) and z_i its charge number. $S(x)$ is a function key, $S(x) = 0$, if $x \leq 0$, and $S(x) = 1$, if $x > 0$. The transport number through the right limit of *j*th volume element is obtained in a similar way.

These expressions are adequate for all of the volume elements in the column, $j = 2$ to $N - 1$, but not for the anode and cathode compartments and their limiting cells and therefore neither for the stirred central compartment. In these cases, the equations must be modified in order to satisfy their specific characteristics, such as the presence of ion-exchange membranes. Thus, the effective transport numbers of proton, $t_{1,am}$, and *i* anion, $t_{i,am}$, through the anion-exchange membrane are, respectively

$$t_{1,am} = t_{1,0} = \frac{\left[f_1\lambda_1 c_{10} S\left(c_{1,0}\right)\right]}{f_1\lambda_1 c_{10} S\left(c_{1,0}\right) + \sum_{i=1}^{n} \lambda_i \left[c_{ij} S(-z_i) S\left(c_{i,j}\right)\right]} \tag{6}$$

$$t_{i,am} = t_{i,0} = \frac{\lambda_i c_{i1} S(-z_i) S\left(c_{i,1}\right)}{f_1\lambda_1 c_{10} S\left(c_{1,0}\right) + \sum_{i=1}^{n} \lambda_i \left[c_{i1} S(-z_i) S\left(c_{i,1}\right)\right]} \tag{7}$$

where $(f_1\lambda_1)$ is the effective molar conductivity of proton through the anion-exchange membrane [19].

In a similar way, the transport number of *i* cation through the cation-exchange membrane, $t_{i,cm}$, is

$$t_{i,cm} = t_{i,N} = \frac{\lambda_i \left[c_{iN} S(z_i) S\left(c_{i,N}\right)\right]}{\sum_{i=1}^{n} \lambda_i \left[c_{iN} S(z_i) S\left(c_{i,N}\right)\right]} \tag{8}$$

Now it is possible to calculate the EM movement of each ion (Table 5, 6) through both walls inside of the *j*th volume and therefore the EM mass balance for *i*th ion in V_j is given by

$$V_j \left(\frac{dc_{ij}}{dt}\right)_{EM} = \left(N_{i,j-1} + N_{i,j+1}\right)_{EM} A = \left(t_{i,j-1} - t_{i,j}\right) \frac{I}{z_i F} \tag{9}$$

3.2.3 *Diffusive transport*

In the ED and DI processes in column, the diffusive mass transport is calculated for the non-ionic and ionic species. The mass balance equation for diffusive transport for non-ionic species is

$$V_j \left(\frac{dc_{ij}}{dt}\right)_D = \left(N_{i,j-1} + N_{i,j+1}\right)_D A = \frac{D_i^*\left(c_{ij-1} - 2c_{ij} + c_{ij+1}\right)AN}{L} \tag{10}$$

where D_i^* is the effective diffusion coefficient ($\approx 10^{-5}$ cm^2 s^{-1}). However, for the cells close to electrode compartments ($j = 1$ and $j = N$)

$$V_1 \left(\frac{dc_{i1}}{dt}\right)_D = \left(N_{i,0} + N_{i,2}\right)_D A = \frac{D_i^*(2c_{i0} - 3c_{i1} + c_{i2})AN}{L} \tag{11}$$

$$V_N \left(\frac{dc_{iN}}{dt}\right)_D = \left(N_{i,N-1} + N_{i,N+1}\right)_D A = \frac{D_i^*(c_{iN-1} - 3c_{iN} + 2c_{iN+1})AN}{L} \tag{12}$$

and for anode and cathode

$$V_0 \left(\frac{dc_{i0}}{dt}\right)_D = \left(N_{i,1}\right)_D A = \frac{2D_i^*(c_{i1} - c_{i0})AN}{L} \tag{13}$$

$$V_{N+1} \left(\frac{dc_{iN+1}}{dt}\right)_D = \left(N_{i,N}\right)_D A = \frac{2D_i^*(c_{iN} - c_{iN+1})AN}{L} \tag{14}$$

When these equations are used to simulate the diffusive transport between the stirred central compartment and one of the limiting compartments through the membrane and boundary layers, the term ($2D_i^*N/L$) is substituted by $k = 8.5 \times 10^{-4}$ h^{-1}, which is the global mass transfer coefficient corresponding to the same resistance to the diffusive transport that the actual system (boundary layer-membrane-boundary layer).

The diffusive transport for ions has been also taken into account. The calculation of the flux of the ionic species has been based in the Fick's first Law and Nerst–Towsend–Einstein relation, because the unidirectional flux of each ion results from a combination of electrical and concentration gradients [20]:

$$N_i = \frac{\lambda_i}{(z_iF)^2}\left[-RT\frac{dc_i}{dy} - z_ic_iF\left(\frac{dE}{dy}\right)_D\right] \qquad (15)$$

where R, T, (dc_i/dy) and (dE/dy) are the gas constant, the temperature (K) and the gradients of concentration and electrical potential due to diffusive transport, respectively. This electric gradient is not imposed externally, but it is present in the ionic solution, due to the small separation of charges which result from diffusion itself. This equation, applied in each volume element to each one of the present ions, may be combined to satisfy the requirement of zero current through all the system $\left(\sum_{i=1}^{n} z_iN_i = 0\right)$.

3.2.4 Chemical equilibria

The values of concentration obtained after transport must not be independent concentrations but they must be constrained by equilibrium. The rapid reactions between species and the reversed reaction, in order to maintain the equilibrium conditions, must be taken into account because these are the principal agents to modify the value of pH and the mobility of the contaminants in the pore medium. Due to this, new concentrations have to be calculated in the jth volume element after each increment of time during the integration of the total transport equations, until the new concentrations agree with the equilibrium values. This is done using the values of concentration obtained from transport and the reaction stoichiometry and chemical equilibria constants. The main chemical equilibria related with the present species and the values of their corresponding constants are shown in Table 5 and 6.

In the experiments where distillated water was used as an assisting agent, an important fraction of Cd, Cu and Pb is present at the beginning as a no mobile solid phase in the studied ash. This is due to the high pH in the aqueous phase, which implies that the metals have a low solubility in water. On the opposite, when ammonium citrate and ammonia solution is used, the initial Cd and Cu transport is highly influenced by their expected dissolution as ammonium complexes, becoming a mobile phase. Here, it has been assumed equilibrium between the solid phase and the aqueous solution. After each increment in time along the process it was checked if solid phases of Cu, Cd, Pb, zinc (Zn), calcium (Ca), etc. are present in each element of volume, in order to establish the value of the local concentration of the different species in the aqueous phase.

In fact, at the end of the operation, insoluble heavy metals are yet in the ash and consequently an important portion of them remain in the solid even after extensive ED or DI cleaning and in spite of high percentage of ash dissolved in some of the experiments.

3.2.5 Complete model

Finally, the complete model consists on the differential equations governing the total transport of the present ions and non-ionic species, as well as the prescriptions for equilibrating the species concentration given by equations of equilibria.

The value of the number of volume element(s) in the column was taken to be five and one for the column and stirred experiments, respectively. Other two additional different volume elements at both ends of the system were regarded as the anode (left), $j = 0$ and cathode (right) $j = \mathrm{N} + 1$ compartments.

The cumulative quantities of contaminants (Cd, Cu, Pb) collected in the electrode compartments were calculated by

$$\frac{dM_A}{dt} = V_0\left(\frac{dc_{i0}}{dt}\right) \qquad (16)$$

$$\frac{dM_C}{dt} = V_{N+1}\left(\frac{dc_{iN+1}}{dt}\right) \qquad (17)$$

Along the calculations, it was continuously checked that the electrical neutrality condition was satisfied for each volume element. Actually, the calculation procedure used guarantees it: In the ED process due to the use of the transport number concept [21, 22] and in the DI process due to both the zero current condition and the initial neutrality of the system.

4 Results

The removal results presented here correspond with the treatments of a MSW incinerator fly ash containing Cd, Cu, Pb and Zn as previously written in the experimental part. General modeling parameters are given throughout Sect. 3. Particular experimental and simulation parameters are shown in Table 1.

In Table 7, experimental and simulated results are compared. Here it is observed that in experiments three and four, where distilled water was used as an assisting agent, the metal content increases after treatment resulting in

Table 7 Experimental and estimated results at the end of the experiments

Test	Experimental content (mg kg^{-1} dry basis)				Calculated content (mg kg^{-1} dry basis)				Experimental removal (%)		
	pH	Cd	Cu	Pb	pH	Cd	Cu	Pb	Cd	Cu	Pb
1	8.6 ± 0.1	29 ± 6	463 ± 14	3034 ± 23	8.2	22	645	3478	65 ± 7	15 ± 3	−15 ± 1
2	9.5 ± 0.1	31 ± 1	486 ± 31	3428 ± 79	9.3	36	403	2754	62 ± 1	10 ± 6	−10 ± 3
3	7.6 ± 0.3	96 ± 8	986 ± 21	3101 ± 180	7.9	92	1263	4310	−17 ± 10	−82 ± 4	−17 ± 7
4	10.6 ± 0.2	133	778	3042	11.4	165	989	3362	−62	−43	−15
5	9 ± 0.1	28 ± 3	272 ± 37	1978 ± 298	9.8	<0.1	<0.1	2398	66 ± 4	50 ± 7	25 ± 11
6	8.9 ± 0.1	38 ± 4	301 ± 33	2089 ± 72	10.1	48	7	2086	54 ± 5	45 ± 6	21 ± 3

negative percentages of removal with respect to the initial ash. This is due to the dissolution of the ash in a higher proportion than the same for the heavy metals during the pre-washing and also during the treatment.

On the opposite, in the experiments 1, 2, 5 and 6 using ammonium citrate/ammonia, at pH values between the initial "natural" fly ash pH ≈ 11.9 and final experimental pHs (8.5–9.5), Cd complexes with the citrate and ammonium from the assisting agent. Cadmium binds, forming complexes as $Cd(Cit)OH^{2-}$ and $Cd(NH_3)^{2+}$ among others. These complexes formation can explain the significant presence of Cd both at anolyte and catholyte due to their charges and the success of Cd removal, not only in the ED experiments with current (one and five) but also in the DI experiments (two and six, no current applied) due to their high mobility. Experimental and predicted values of Cd removal at the end of the experiments are very similar, allowing the assumption that the more important Cd species are considered in the model.

Copper only shows adequate removal in experiments five and six. This reflects that using 0.25 M ammonium citrate in 1.25% ammonia as assisting agent to form Cu complexes [$Cu(NH_3)_4{}^{2+}$ or $Cu(NH_3)_3OH^{+}$], as in experiments 1, 2 and 6, is not enough to obtain a satisfactory Cu removal. Thus, to promote Cu removal it is necessary to increase the mobility of Cu species by mean not only of current, but also by stirring combined with a high assisting agent/ash ratio (L/S = 4).

In the experimental conditions Cu is forming basically positive ionic complexes and shows, experimentally and by modeling, a clear tendency to move towards the cathode compartment.

Lead only shows some removal in experiments with ammonium citrate as assisting agent in stirred systems (L/S = 4) with and without current (experiments five and six).

5 Conclusions

Cadmium, when combined with 0.25 ammonium citrate in 1.25% as assisting agent, is highly mobilized (experiments 1, 2, 5 and 6). When distilled water is applied, Cd shows almost no removal. These results agree with the predicted by modeling and attest the efficiency of 0.25 M ammonium citrate as assisting agent for removing this metal from fly ashes.

Copper is efficiently removed from fly ashes with ammonium citrate and stirring and also Pb is removed in some extension in these same conditions.

The models produces values of removal in agreement with the experimental results and also reproduces satisfactorily the experimental pH values and the evolution of metals not included under the heavy metal category (Na, Ca, Al, Zn, etc.) present in the complex system that fly ash constitute, moreover in the presence of assisting agents.

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