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Abstract: Electrodialytic remediation (EDR) is a technique in which contaminants are removed from waste material by applying an electric field which forces their movement into concentration chambers through ion-exchange membranes. In the current work EDR is used for the treatment of heavy metal–contaminated fly ash. The objective is to study the impact of major constituents of fly ash on remediation times, on efficiency, and on the performance of membranes. The results show that major constituents foul the ion-exchange membranes, decreasing their ability to transport metal ions out of the waste compartment.

Keywords: Heavy metal, fly ash, ion-exchange membranes, electrodialytic remediation

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INTRODUCTION

Electrodialytic remediation (EDR) is a technique in which contaminants are removed from a waste material by applying an electric field which forces them to “move out” of the waste. EDR technique uses selective ion-exchange membranes to separate the waste from the solutions where contaminants are to be collected. These membranes are charge selective: positive ions (cations) are allowed to cross cation-exchange membranes, while anion-exchange membranes allow the passage of negative ions (anions). In EDR, the cation-exchange membrane is placed between the waste and the cathode (negative electrode), so that the positive ions moving in the direction of the electrode can leave the waste and be collected in the solution near the cathode (see Fig. 1). An anion-exchange membrane is placed between the waste and the anode (positive electrode) so that anions moving in the direction of the anode can leave the waste and be collected at the solution on the anode side (general principles of electrodialytic remediation technique has been described elsewhere) (1, 2).

EDR has recently been applied to the treatment of heavy metal–contaminated fly ash from the incineration of municipal solid waste (3–6). Fly ash is a granular, fine powder enriched in the more volatile heavy metals. It is considered hazardous waste due to the leaching of heavy metals and the presence of some organics (7). During previous treatment of this waste by EDR, large amounts of heavy metals were found on the ion-exchange membranes separating the waste from the electrodes (3) with possible implications on remediation efficiency. A following study conducted on the retention of heavy metals at ion-exchange membranes during EDR (8) confirmed high retentions at the membranes and showed the influence of the pH electrolytes in concentration compartments.

Characterization of MSW fly ash has shown the presence of highly soluble substances, such as calcium carbonates, sodium and potassium chlorides, and sulfates (9). Despite the fact that these are major constituents of fly ash, representing more than 60% of its mass (while interest heavy

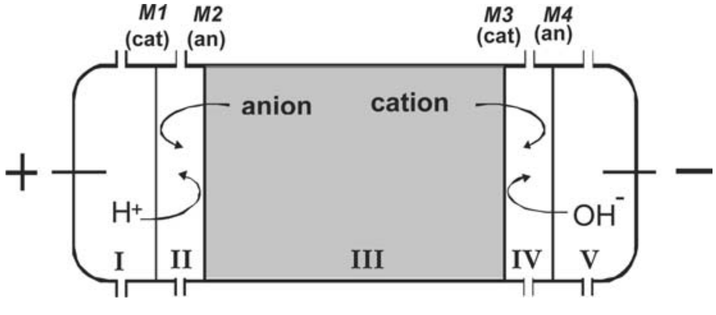

Figure 1. Principle of electrodialytic remediation.

metals represent less than 1%), no study has been conducted so far on how these major constituents affect EDR of fly ash. Taking into consideration their characteristics (such as electric charge, size, and ability to dissolve) and the fact that they are present in large amounts, major constituents might be transported preferentially compared to the heavy metals or compete with those for the complexing agent used to improve dissolution of metals. It is therefore expected that the major constituents of fly ash will influence the efficiency, the duration, and even the viability of EDR of heavy metals from fly ash.

The present work focuses on the influence of major constituents of fly ash on EDR, including aspects such as remediation time, remediation efficiency, and retention at the membranes. The electrodialytic remediation is applied to two different types of solutions: (1) a solution containing both metals and high concentrations of salts obtained by dissolution of fly ash; and, (2) a solution in which practically only the metals are present, made up by dissolving reagent-grade metal salts. Both solutions also include sodium-gluconate as complexing agent. The comparison between the two allows identifying the impact of the major constituents of fly ash on EDR.

MATERIAL AND METHODS

Preparation of Solution from Fly Ash

In this experiment 20 g of fly ash were mixed with 125 mL of 0.2 M HNO_3 in a plastic flask. Sodium-gluconate 4% was added ($V = 375$ mL) as an assisting agent. The flask was then agitated for 48 h, during which concentration of sodium-gluconate is 3% and liquid-to-solid ratio (L/S) is 25. At the end, pH was measured and the remaining solid material was removed by filtration through a 0.45 μm pore-membrane. The volume was then made up to 500 mL with distilled water. Conductivity, pH, and concentrations of Pb, Zn, Cu, and Cd were measured and the solution was kept for electrodialytic treatment.

Preparation of Heavy Metal Solution

The preparation of the heavy metal solution was done in two steps. In the first, a concentrated solution of heavy metals was prepared by dissolving the corresponding metal salts in water. The second step consisted in diluting the concentrated solution of heavy metals to the same concentration as in the solution from fly ash, while at the same time adding the assisting agent and adjusting pH.

For the preparation of the concentrated solution 0.274 g of zinc sulphate ($ZnSO_4 \cdot H_2O$), 0.144 g of lead nitrate (N_2O_6Pb), 0.021 g of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, and 0.0052 g of cadmium chloride ($CdCl_2 \cdot H_2O$) were introduced in a 500-mL flask and the volume was made up to the mark with distilled water.

In the second step, 125 mL of the concentrated solution was introduced in a 500 mL flask, together with 15.00 g of sodium-gluconate. pH was adjusted to 11 with NaOH and distilled water was added to the mark. Final concentration of sodium gluconate is 3%, which is the same as in the fly ash solution.

Electrodialytic Experiments

The cell used for the electrodialytic treatment consists of a Plexiglas cylinder (4 cm in diameter) divided transversely into five compartments (I, II, III, IV, and V) which are separated by ion-exchange membranes (see Fig. 1). M1 and M4-membranes prevent substances moving in the electric field to get to the electrodes and be oxidized/reduced there. For instance the oxidation of chloride at the anode produces toxic chlorine gas ($2Cl^- \rightarrow Cl_2 + 2e^-$) while the reduction of metals cations on the cathode leads to "elemental" metal deposits on the surface of the electrode, which can grow inside the cell to an intolerable size. M2 and M3 are anion and cation-exchange membranes, respectively, used both to prevent substances in the electrolytes II and IV of moving into III under the influence of the electric field, and to allow contaminants in III to be removed into II or IV. Inert electrodes are placed at both ends.

The sample solution was introduced in chamber III (150 mL for experiments with heavy metal solution and 100 mL for experiments with fly ash solution), and $NaNO_3$ (0.01 M) was used as electrolyte in chambers I, II, IV, and V (the volume of $NaNO_3$ used was 200 mL in chambers I and V and 100 mL in chambers II and IV). During the experiments sample and electrolyte solutions were recirculated between the cell compartments and glass flasks using multichannel peristaltic pumps and a low-voltage direct current (50 mA) was applied at the electrodes. Voltage drop across the cell was read regularly. After the experiment the cell was dismantled and all solutions collected. Membranes and electrodes were put in 5 M nitric acid over night and the solutions kept. All solutions were filtered through a 0.45 μm membrane and acidified (with nitric acid) to pH 2 for preservation. Metal concentrations were determined by atomic absorption spectroscopy in flame using a Perkin Elmer 5000 AAS.

The heavy metal solution (HV) was used in three electrodialytic experiments with different remediation times: 4 h, 8 h, and 12 h. During these experiments pH was not adjusted. An additional 4 h experiment was made during which sample's pH in compartment III was adjusted to 11. The fly ash solution (FA) was used once in an EDR experiment conducted until conductivity in central compartment was low. Summary of experimental conditions is presented in Table 1.

Table 1. Electrodialytic remediation experiments

Experiment	Sample	Duration of experiment	Electric current (mA)	pH during experiment
HV-4	Heavy metal solution	4 hours	50	Not adjusted
HV-8		8 hours	50	Not adjusted
HV-12		12 hours	50	Not adjusted
HV-4a	Heavy metal solution	4 hours	50	Sample pH adjusted to 11
FA	Fly ash solution	Not predefined	50	Not adjusted

RESULTS AND DISCUSSION

The amount of metal present in the solution to be treated (which was introduced in the central compartment of the electrodialytic cell at the beginning of each experiment) is presented in Table 2. Solutions HV-4 to HV-12 were prepared so that the metal amount would be the same order of magnitude as when the fly ash extractant (FA) was used. The remainder of this section is divided into three parts. The first part presents the results of the EDR experiments with the heavy metal solution for different times: 4 h, 8 h, and 12 h. The second part compares the experiment in which the sample's pH was adjusted to 11 to the experiment without pH adjustment (HV-4 and HV-4a). Finally, the third part compares the fly ash solution and the heavy metal solution.

Electrodialytic Remediation of Aqueous Solutions of Heavy Metals

This section presents the results of EDR experiments HV-4, HV-8 and HV-12. Figure 2 represents the amount of heavy metal in central compartment after 4, 8, and 12 h of EDR. As the time of remediation increases the amount left in III decreases, as expected, with a step between the fourth and the eight hours. This time interval coincides with a pH of 7.5–8 in chamber III (Fig. 3).

Table 2. Metal amount (mg) present in solution in central compartment at the beginning of each experiment

Experiment	Zn	Pb	Cu	Cd
HV-4	6.76	5.8	0.40	0.11
HV-8	6.03	5.4	0.37	0.14
HV-12	5.39	4.5	0.34	0.13
HV-4a	5.95	5.4	0.36	0.13
FA	7.3	6.4	0.66	0.24

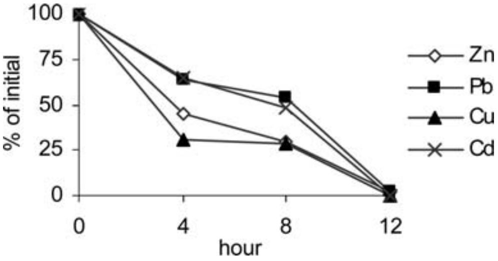

Figure 2. Amount of heavy metal found in central compartment after 4, 8, and 12 h of EDR, expressed as percentage of initial amount.

Copper is the most easily removed metal (after 4 h only 31% of initial amount is left in III), followed by zinc (45% left after 4 h). Cadmium and lead present the slowest removal, with approximately 64% still remaining in central compartment after the initial 4 h. After 12 h of EDR practically all the metals were removed: the percentage of initial amount still in sample compartment by then was 2.0% for zinc, 3.5% for lead, and 0% for both copper and cadmium.

The distribution of zinc, lead, copper, and cadmium for 0, 4, 8, and 12 h is presented in Fig. 4. At zero hours all the metals are in chamber III. As experiments proceed in time metals are removed from this chamber and start to appear in adjacent compartments and membranes. Zinc and lead appear on both sides of the cell (anode and cathode). Copper moves only toward the anode, with less than 3% being found on the cathode side after 12 h. Cadmium moves mainly to the cathode side during the first 8 h, appearing also on the anode side (23%) in the 12 h experiment. The different behavior of these metals gives an indication on their speciation. Probably all copper compounds existing in the solution are negatively charged (e.g., $[Cu(gluconate)_2(OH)]^-$, $[Cu(gluconate)_2(OH)_2]^{2-}$, and $[Cu_2(gluconate)_2(OH)_4]^{2-}$) and therefore copper movement is always toward the anode, whereas zinc, lead, and cadmium are present both as negatively and positively charged species.

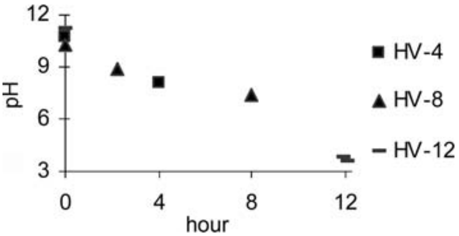

Figure 3. pH in compartment III during EDR experiments with heavy metal solutions.

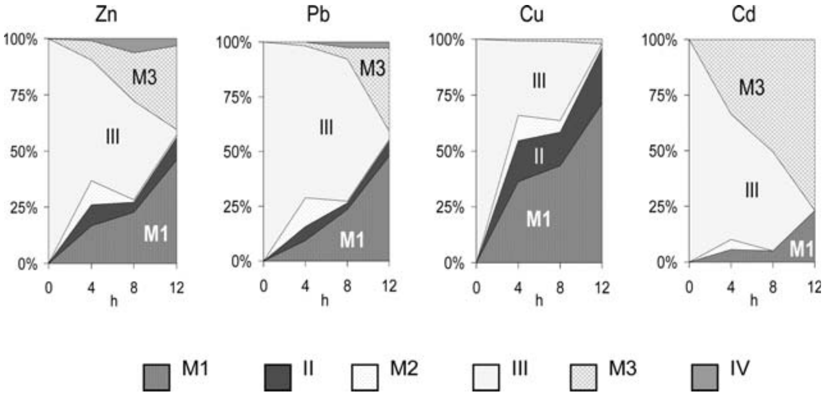

Figure 4. Heavy metal distribution (%) in EDR experiments HV-4 to HV-12 (no metal was found in chamber V nor on membrane M4).

Of the amount of metal moving in the direction of the anode, more than half is found on the *M1* membrane and the rest is found in solution II. This is expected since *M1* is a cation-exchange membrane, used to prevent anionic substances from moving into I. The M2-membrane does not seem to retain the metals: although some metals do appear in this membrane after 4 h, they disappear after, and at 12 h no metals are found here.

The *M3*-membrane, however is practically impermeable to the cations moving in the direction of the cathode, as almost no metals appear in chamber IV while large amounts appear on the *M3*-membrane. A similar behavior was seen in previously reported EDR experiments with fly ash extractant (8) where this was related to the high pH in chamber IV. In the present experiments pH in chamber IV is also high (Fig. 5).

Effect of Adjusting pH in Central Compartment During EDR

This section compares two experiments conducted with the heavy metal solutions HV-4 and HV-4a. The difference between the two is that in

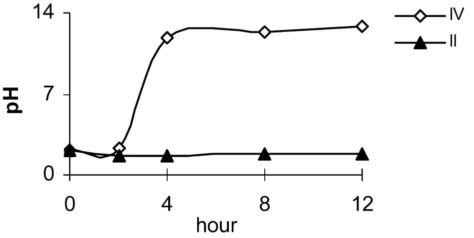

Figure 5. pH in chambers II and IV during EDR experiments with heavy metal solutions.

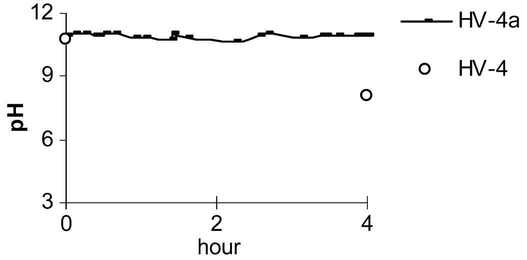

Figure 6. Evolution of pH with time in EDR experiments HV-4 and HV-4a in central compartment.

HV-4a sample's pH was continuously adjusted to 11, whereas no pH adjustment was done in HV-4, resulting in this last case in acidification of the sample from an initial value of 11 to a final value of 8 (Fig. 6).

The effect of adjusting sample's pH on remediation can be seen in Fig. 7, which shows the distribution of metals after 4 h when pH is not adjusted (HV-4) and when pH is adjusted (HV-4a). This figure shows that the amount of zinc, lead, and cadmium left in III (not removed) is higher when pH is not adjusted (HV-4). This is expected, since around pH 8 these metals have lower solubilities than at pH 11 (Fig. 8), which means that as pH decreases these metals partially precipitate and remain in III. For copper the removals are similar in both experiments, and this reflects the fact that copper solubility at pH 8 is similar to that at pH 11.

Looking at the speciation of the metals it can be seen that when the sample's pH is around 11, no metals are found in the compartments and on membranes on the cathode side. At this pH all metals move toward the anode and are therefore negatively charged. When sample's pH decreases from 11 to 8 small amounts of zinc and cadmium appear on the cathode

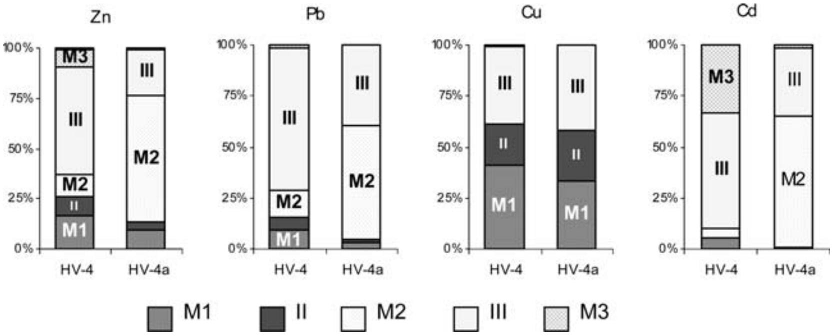

Figure 7. Distribution of Zn, Pb, Cu, and Cd at the end of EDR experiments HV-4 and HV-4a (no metal was found in chambers I, IV, and V nor in membrane M4).

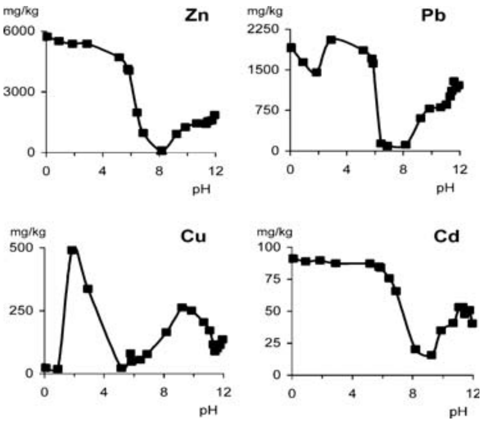

Figure 8. Metal extracted from MSW-APC fly ash (mg/kg of ash) at different pH in batch tests using 3% sodium-gluconate solution (L/S = 25) (In: Ferreira et al., 2004b).

side (*M3*-membrane), which means that as pH decreases some positively charged forms of these metals appear.

Impact of Major Elements on EDR of Heavy Metal Contaminated Fly Ash

Experiment FA was conducted for 24 h, when conductivity in central compartment was approximately zero, indicating that dissolved substances present in sample compartment had been removed. This coincides with a voltage increase around this time. Figure 9 shows the time evolution of these parameters in experiment FA and when major elements are not present (HV-12). It can be seen that conductivity inside III at the beginning was approximately three times higher in FA than in HV-12. This is because FA solution contains

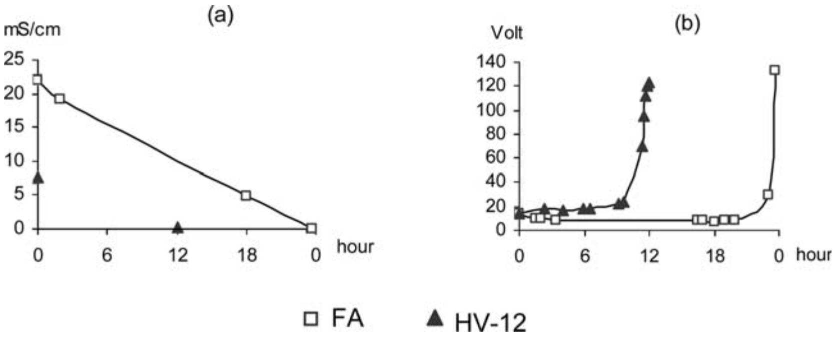

Figure 9. Time evolution of (a) conductivity in III and (b) voltage drop across the cell in EDR experiments FA and HV-12.

larger amounts of soluble salts (dissolved from the ash) leading to a higher conductivity. Figure 9 also shows that the time necessary to completely remove substances from chamber III was double when salts are present (FA) than when they are not present: in the first case it took almost 24 h for the experiment to end, while in the second it took only half of that (12 h).

The decrease with time of metal remaining in sample can be seen in Fig. 10 for both experiments. This shows that metals are removed from the very beginning in both cases, but when salts are present removal rate is higher at the end of the experiments than at the beginning, probably because the electric field is carrying the more mobile salts first. Nevertheless, in both FA and for HV-12 practically all the metals were removed: the percentage of metals still in the sample compartment at the end was, respectively, 2.0% and 2.7% for zinc, 3.5% and 1.7% for lead, and 0% for copper and cadmium in both experiments.

The metal distribution at the end of both experiments is presented in Fig. 11. It can be seen that when major constituents of fly ash are not present (HV-12) metals cross the M2-membrane into II and then are collected on M1-membrane. When these major constituents are present (EDR experiment FA) metals appear on the M2-membrane, with smaller amounts in II and M1-membrane.

The *retention of metal* by a membrane is the percentage of metal trying to cross that membrane under the electric field, and failing to do so, consequently being found in/on the membrane at the end of EDR. Values of the retention by the M2-membrane are presented in Fig. 12. It can be seen that values are less than 2% in experiment HV-12 (where major elements are not present), while increasing considerably for experiment FA.

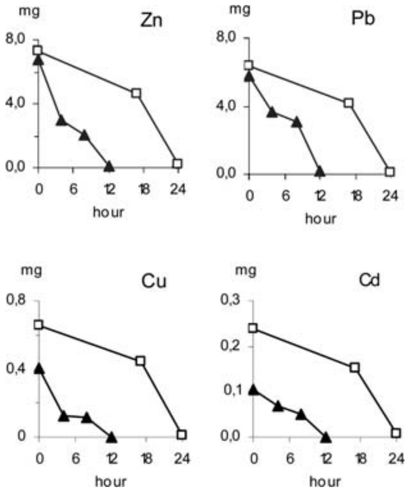

Figure 10. Evolution of metal in solution III for EDR experiments. HV-12 (-▲-) and FA (-■-).

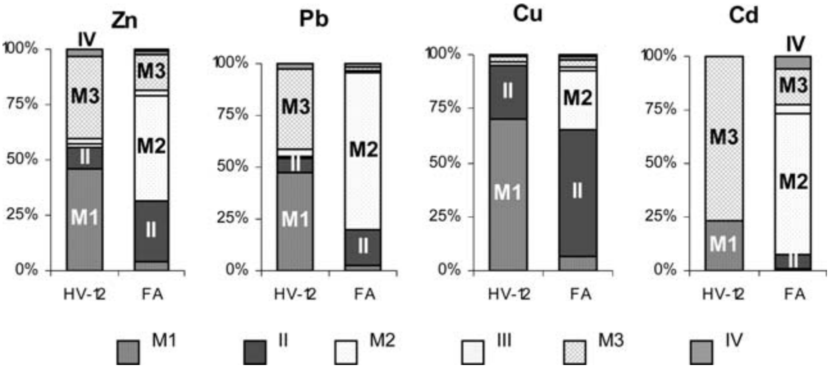

Figure 11. Metal distribution (percentage of total) at the end of EDR experiments HV-12 and FA (no metal was found in chamber I and V nor in membrane M4).

In a previous study on the retention of heavy metals at ion-exchange membrane (8) it was suggested that pH differences of solutions on both sides of the membrane might be responsible for high retention values. However, based on the present results an additional explanation can also be put forward: the presence of large amounts of substances dissolved from the ash might foul the membrane, increasing retention. This would explain the much higher retention for FA than for HV-12.

Looking at retention values for M3-membrane in Fig. 12 it can be seen that these are high in both experiments. For the M3-membrane the important factor conditioning the retention is probably the high pH inside chamber IV, which provokes the precipitation of metals, as suggested in (8).

CONCLUSION

Complete remediation of both types of samples was possible with EDR, withless than 3.5% of the initial amount of zinc and lead and 0% of

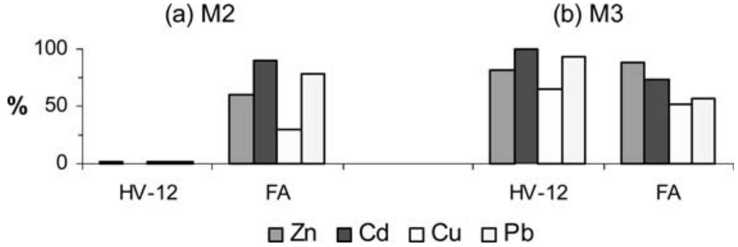

Figure 12. Retention of metals (%) by the membranes placed on each side of sample compartment: (a) M2 (anion-exchange membrane); (b) M3 (cation-exchange membrane).

cadmium and copper still remaining in sample at the end of remediation experiments.

Comparison between two 4 h EDR experiments in which the sample's pH was adjusted to 11 and not adjusted, showed higher remediation when sample's pH was kept high. This shows that choosing the right pH-range for the sample's pH is important, since pH ranges where solubilities are the lowest can be avoided.

Comparison between EDR experiments conducted using as sample a solution with heavy metals or a solution with heavy metals plus major constituents of fly ash showed that when major constituents are present the remediation takes twice as long. This happens because major constituents are also dissolved and part of the current is used on their transport across the cell, increasing the amount of time necessary for remediation and decreasing current efficiency.

Regarding the retention in/at the ion-exchange membranes there were two main findings. First, retention by the anion-exchange membrane (M2) separating chambers II and III is much higher when major constituents of fly ash are present (between 50–100%), then when only metals are present (less than 2%). This is associated with membrane fouling due to large amounts of salts present. Second, retention by the cation-exchange membrane (M3) between III and IV is high, regardless of the presence or not of major constituents of fly ash. The M3 membrane is in same cases practically "impermeable" to the cations moving toward the cathode, and the reason for this may be associated to the high pH in chamber IV. Major constituents of fly ash have therefore a direct impact on remediation of heavy metals from fly ash using the EDR technique: they increase remediation time and fouling of the ion-exchange membranes, decreasing their ability to transport metal ions out the waste compartment. This result suggests that a possible improvement of EDR technique would be to wash the MSW fly ash prior to treatment: removing major constituents from the fly ash would most probably be beneficial and lead to better removal efficiencies.

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